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Scientific Applications of Infrared Synchrotron Sources

Michael C. Martin

Advanced Light Source, Lawrence Berkeley National Laboratory

Outline

- ⇒ Why use a synchrotron?
- ⇒ Current synchrotron infrared programs
- ⇒ Far-IR (THz) science directions

MCMartin@lbl.gov

<http://infrared.als.lbl.gov/>

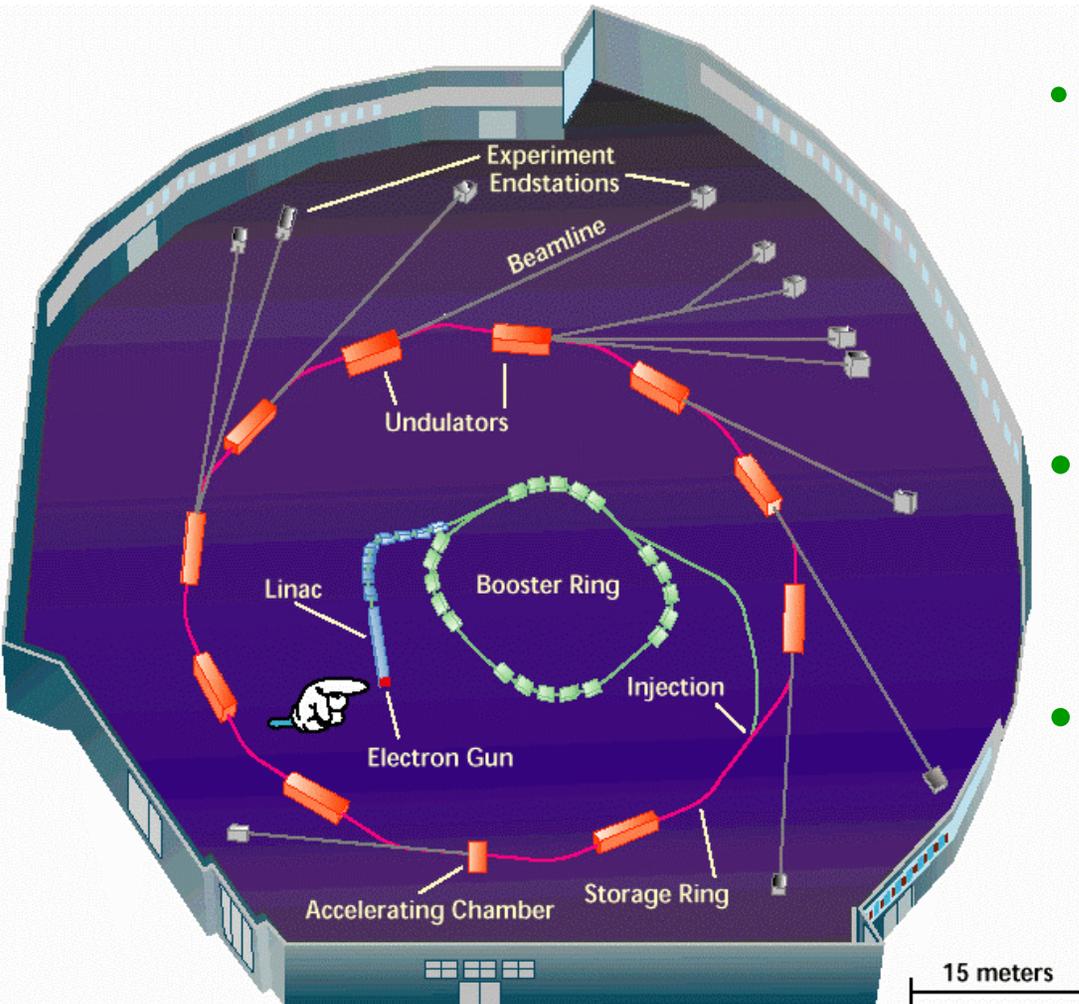
Supported by:

Office of Science, Materials Science Division, U.S. Department of Energy (DOE)



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Why use a synchrotron for IR?



• High brightness

- Essentially a point source
- Can focus light to a diffraction-limited size:
[Microscopy](#)

• More far-IR flux

- Smaller samples
- Better signal-to-noise

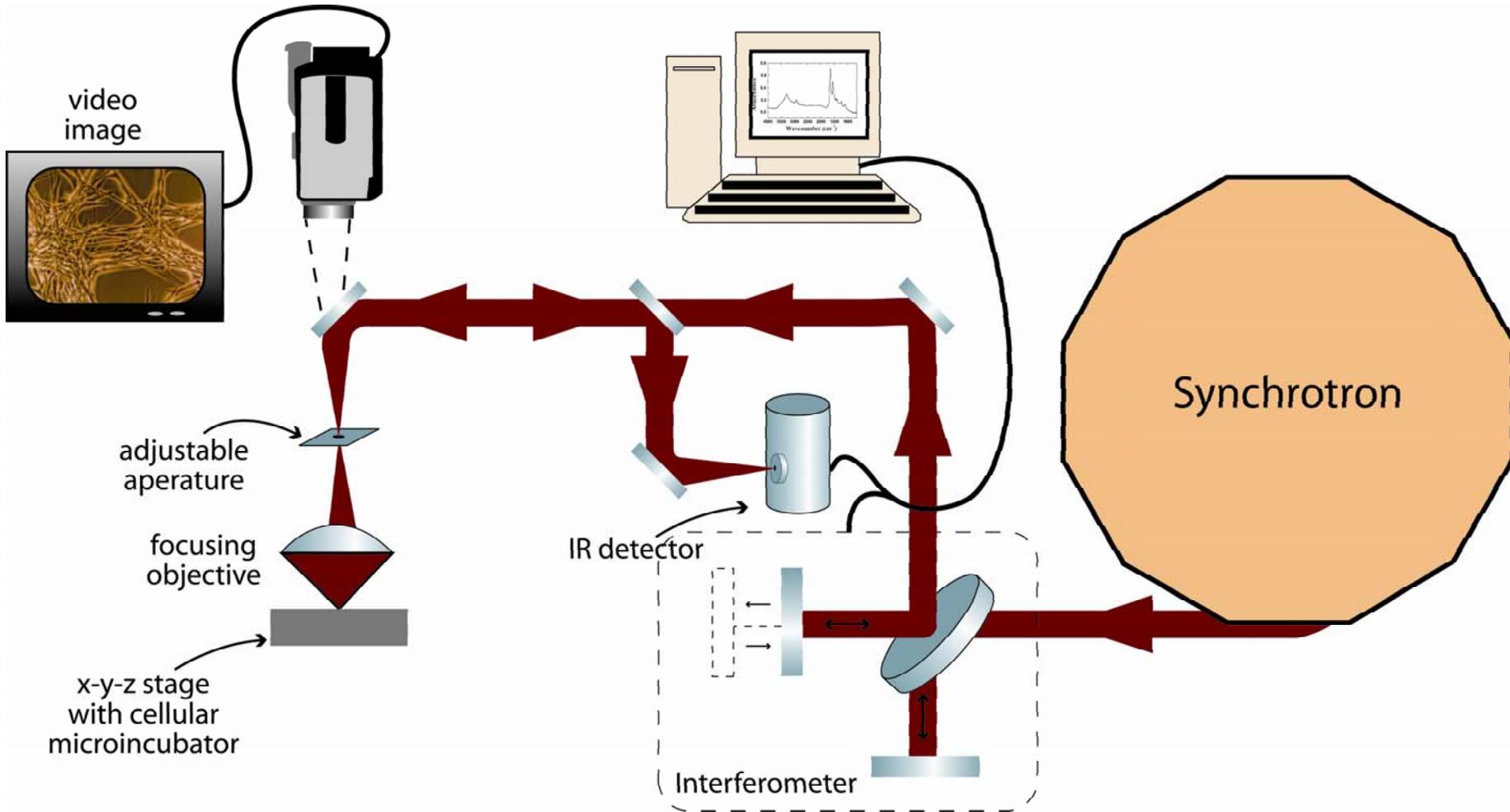
• Pulsed source

- Light is from electron bunches
- Fast timing measurements (nsec)



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Synchrotron-based FTIR Spectromicroscopy

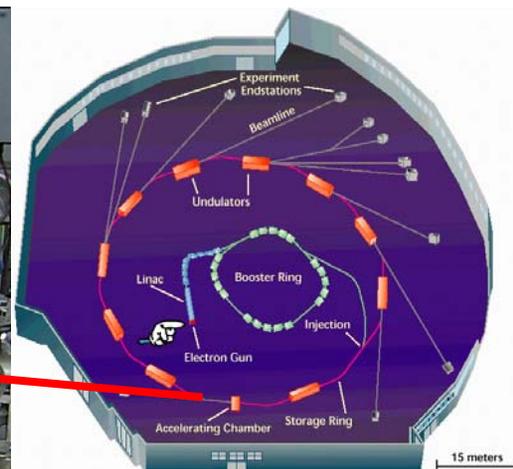


<http://infrared.als.lbl.gov/>



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Synchrotron-based FTIR Spectromicroscopy



Nicolet Continuum IR microscope Nicolet 870 FTIR Bench

SR-FTIR is a non-destructive, bioanalytical imaging technique with a 3-10 micron spatial resolution. With it, one can simultaneously track multiple chemical signatures.

<http://infrared.als.lbl.gov/>



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ALS Beamline 1.4.3 FTIR Spectromicroscopy



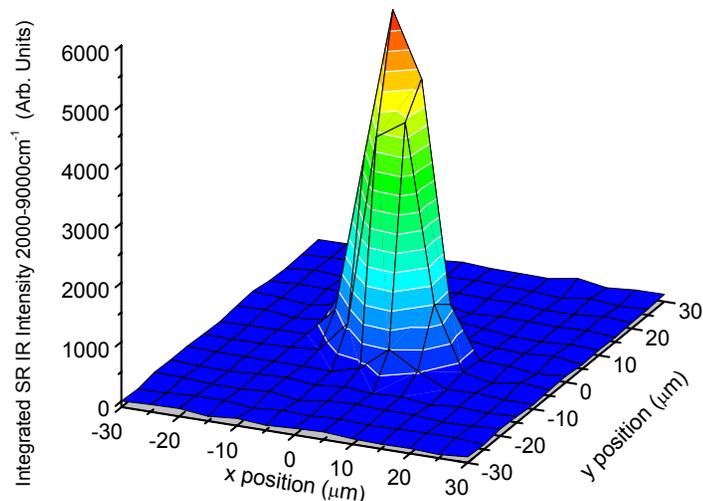
Nicolet 760 FTIR Bench Nic-Plan IR Microscope

Applications:

- Single living cells, toxic contaminants, protein microcrystals, rhizoids, water jets, forensic evidence, corroded metals ...

<http://infrared.als.lbl.gov/>

- **3 – 10 μm spot size**
- Microcooler stage (70 - 740K)
- Grazing incidence & ATR objectives
- Autofocus capabilities

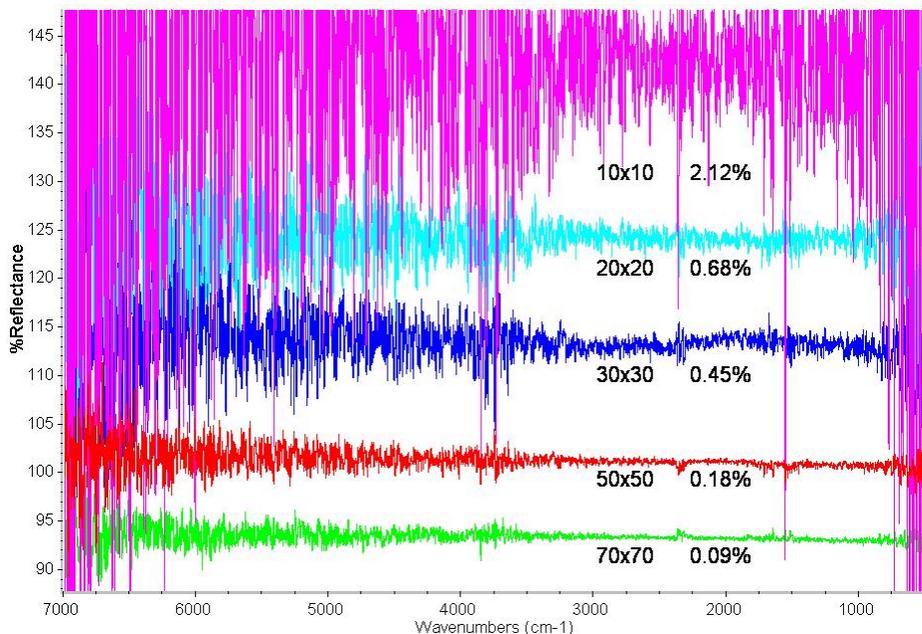




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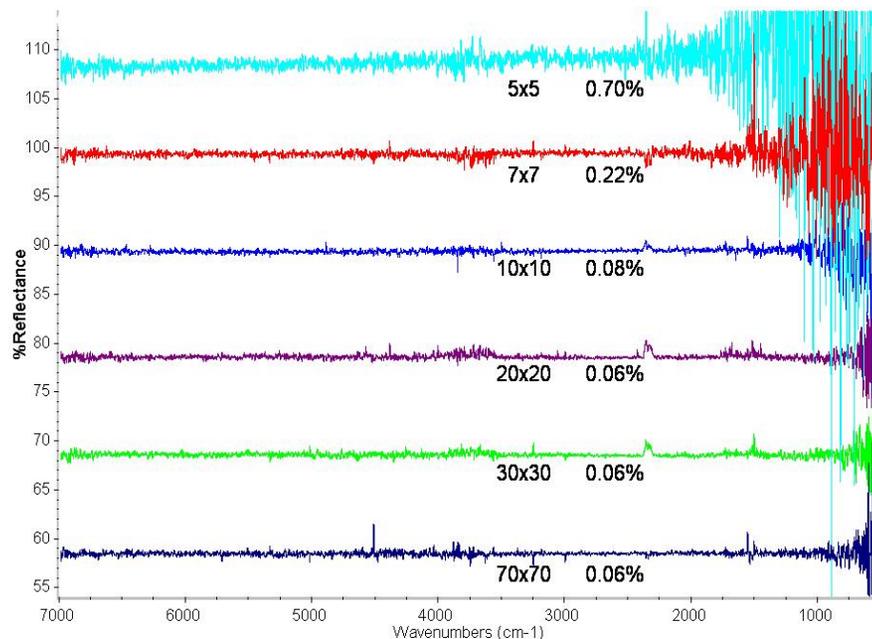
Why Synchrotron IR Source? High Brightness.

Thermal IR source



100% reflectance lines showing the noise level of the EverGlo™ thermal IR source when using smaller and smaller apertures. Noted for each curve are the aperture dimensions and the RMS noise determined between 2450 and 2550 cm^{-1} .

Synchrotron IR source

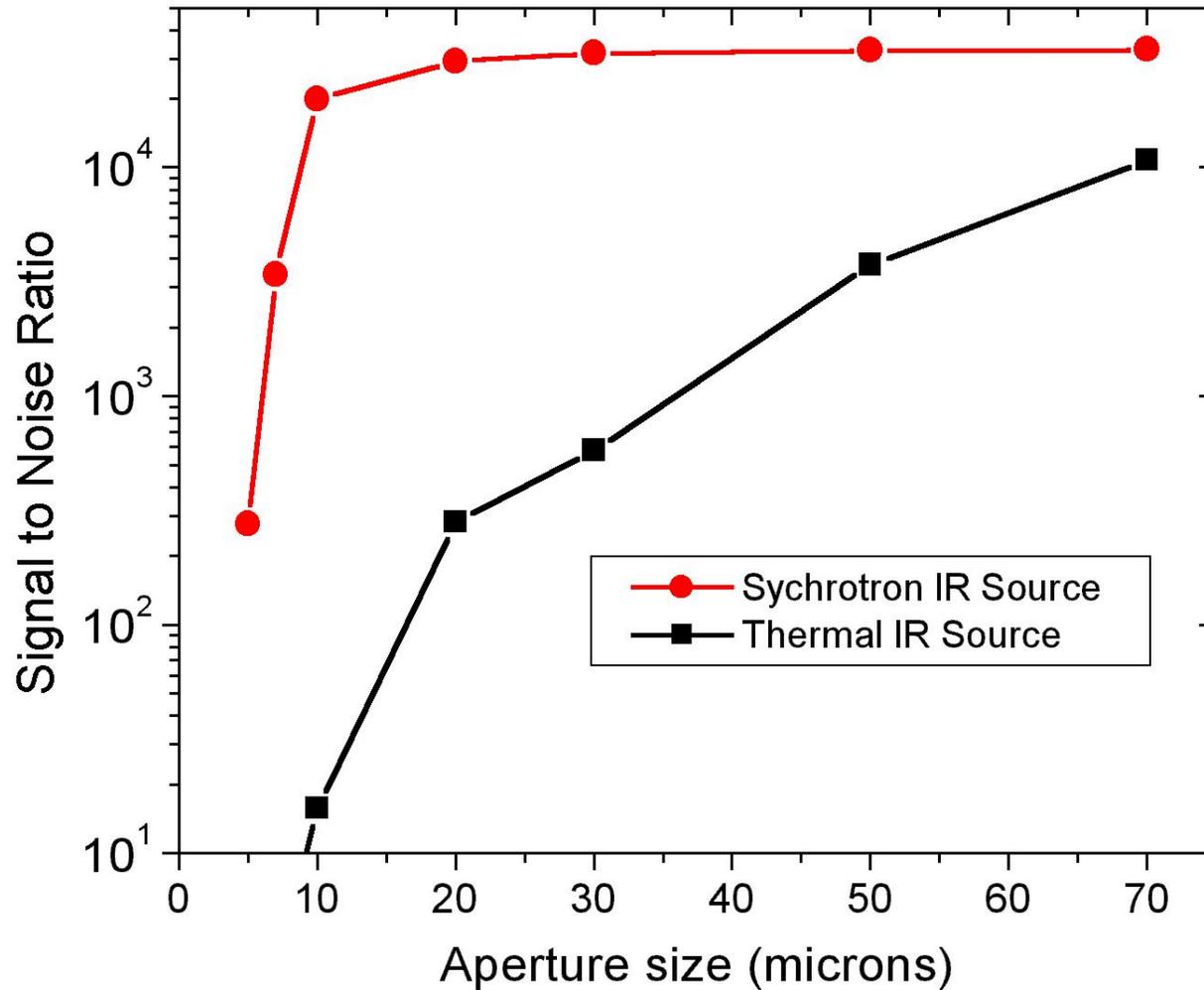


100% reflectance lines for the ALS synchrotron IR source when using smaller and smaller apertures. Noted are the aperture dimensions and the RMS noise determined between 2450 and 2550 cm^{-1} . The diffraction-limited synchrotron spot size is not clipped until the aperture is below 10 microns, and only for the longer wavelengths.



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High Brightness of Synchrotron Source





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ALS Beamline 1.4.2 FTIR Spectroscopy



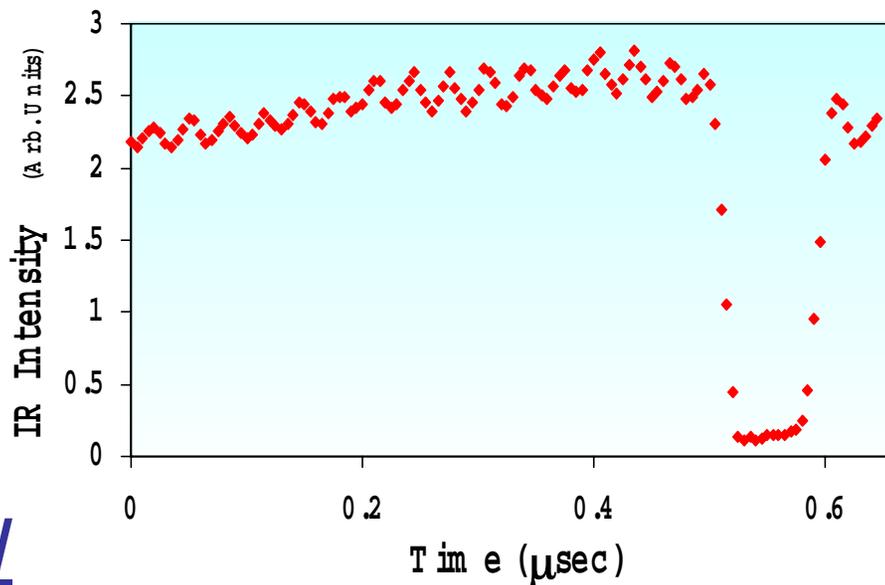
Bruker *IFS 66v/S*

Applications:

- Strongly correlated electron systems, surface chemistry, pump-probe dynamics, corroded metals, ATR cell, ...

<http://infrared.als.lbl.gov/>

- 15 - 25,000 cm^{-1} range
- LHe cryostat (1.6 – 475 K)
- 5 ns fast timing capabilities



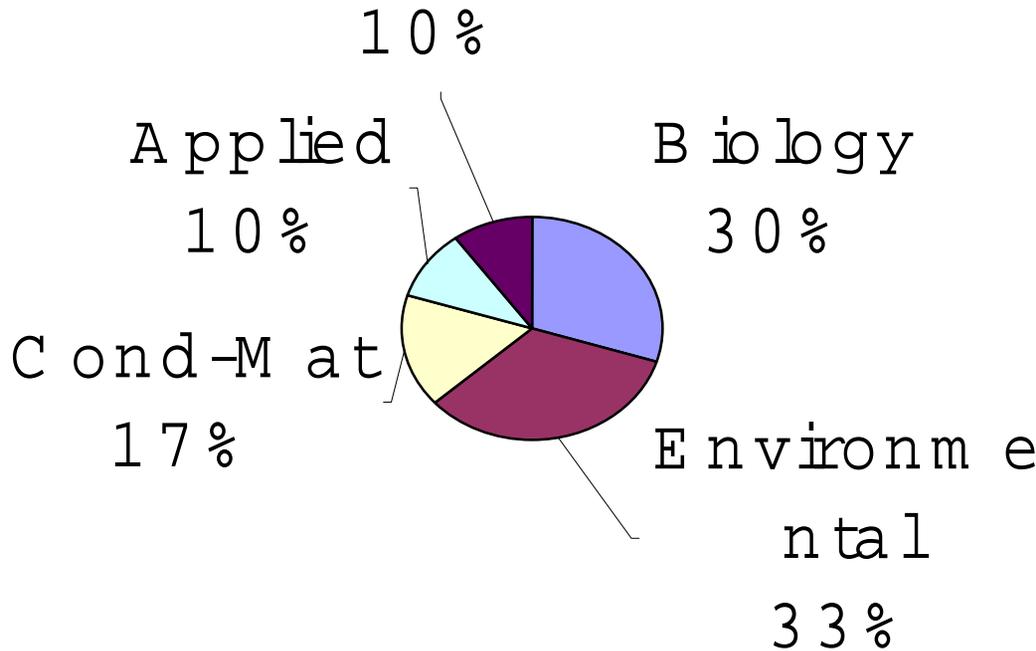
Presently Active User Groups at the ALS IR Beamlines

- Benning, Lianne
- Borch, Thomas
- Breunig, Thomas
- Dudley, Donald

- Univ. of Leeds
- Montana State
- UCSF
- Science Institute

- Cyanobacteria & silification
- Binding in humic substances
- Dental research
- Photocycle of PVD

Other ALS IR Users (2002)



- Perry, Dale
- Saykally, Richard
- Sims, Ronald
- Sigee, David
- Yano, Junko

- LBNL, ESD
- UCB Chemistry
- Utah State Univ.
- Univ. of Manchester
- LBNL, PBD

- Forensic samples
- Liquid microjets & near-field
- Biodegradation in soils
- Biodiversity in phytoplankton
- Photosystem II

Individual Human Cell Responses Studied by Synchrotron Infrared Spectromicroscopy

Hoi-Ying N. Holman, *Center for Environmental Biotechnology*
Michael C. Martin, **Wayne R. McKinney**, *Advanced Light Source Division*
Eleanor A. Blakely, **Kathy Bjornstad** *Life Sciences Division*
Regine Goth-Goldstein, **Marion L. Russell** *Environmental Energy Tech. Division*

Supported by

**Director, Office of Science, Office of Basic Energy Sciences,
Materials Science Division of the U.S. Department of Energy (DOE),
under contract #DE-AC03-76SF00098**
**Army Corps of Engineers of the U.S. Department of Defense (DOD), and
the U.S. National Aeronautics Space Administration (NASA)**

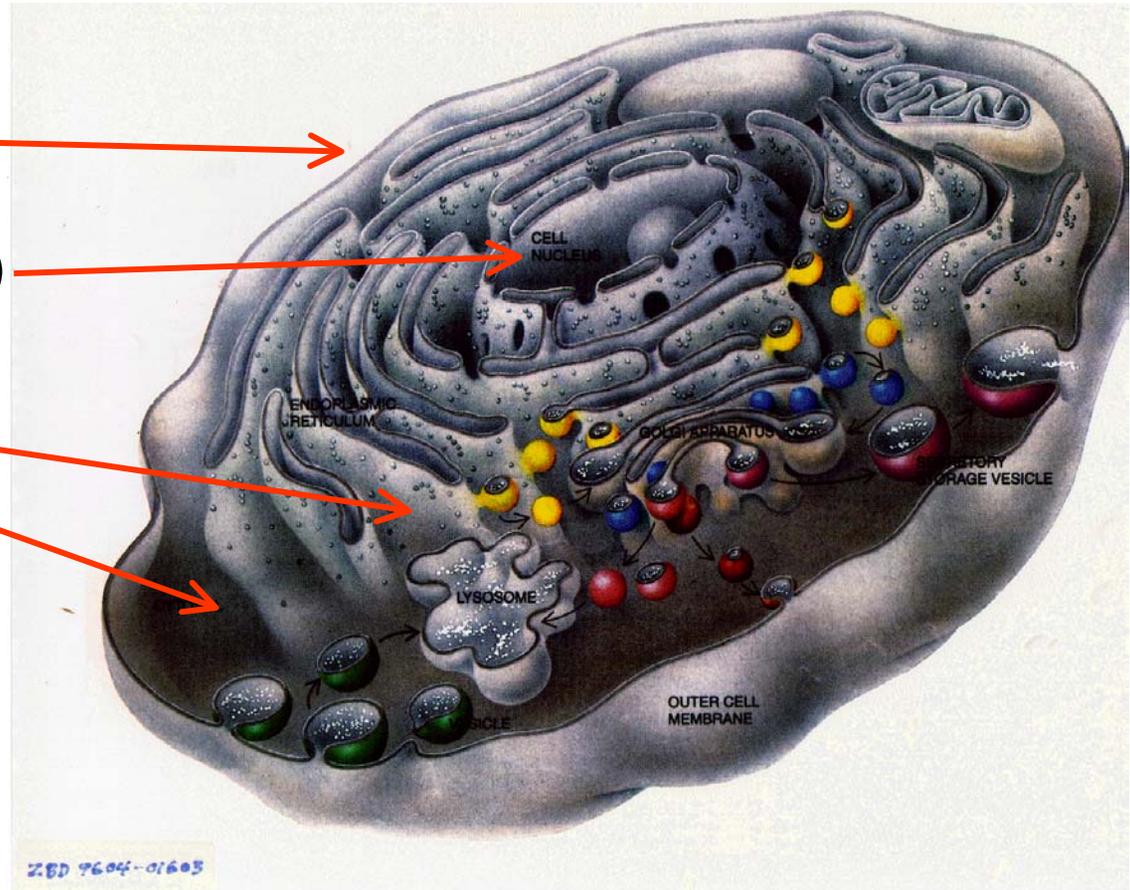


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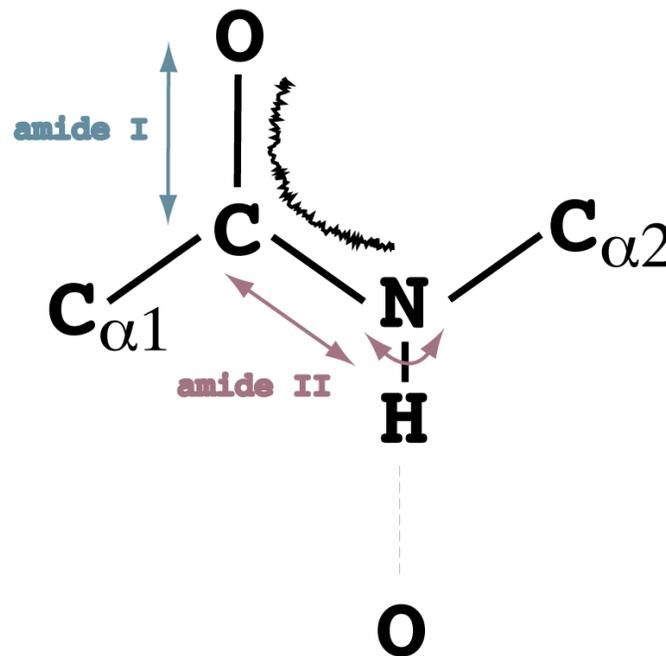
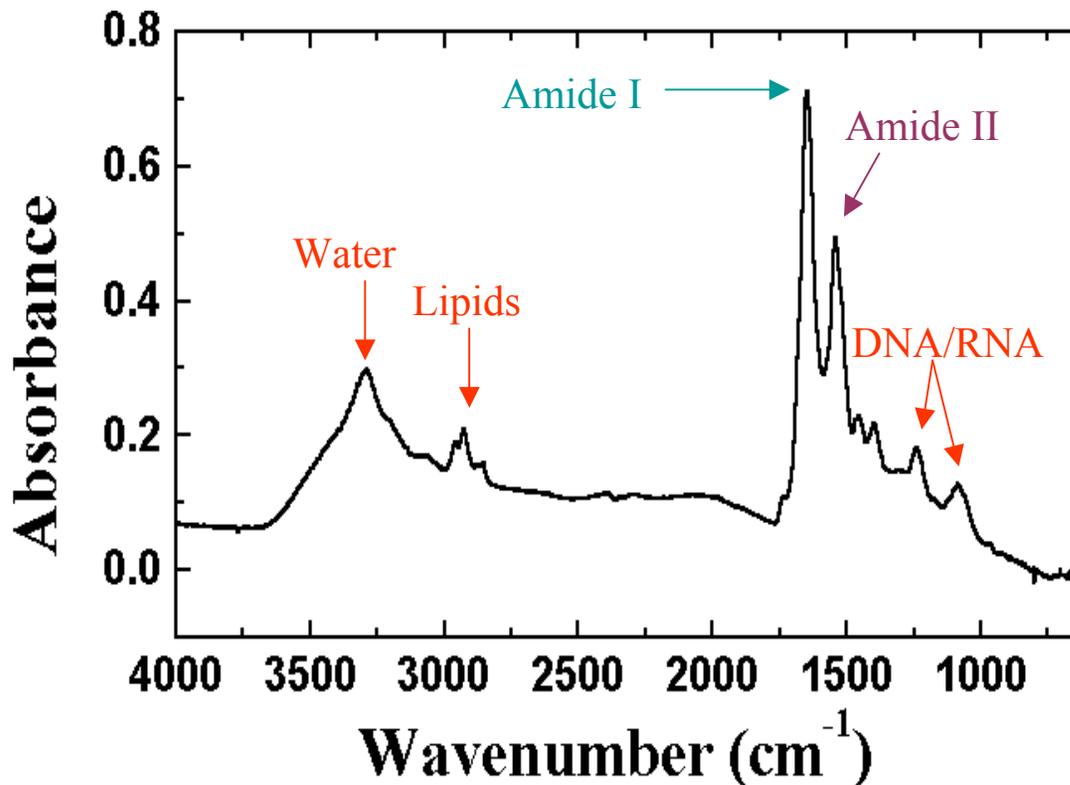
Infrared Spectromicroscopy of Individual Living Cells

Infrared spectra are obtained from individual living cells.

- Lipids (cell walls)
- Nucleic acids (DNA, RNA)
- Proteins
- Each of these major classes of cellular components have distinct IR markers



Example infrared spectrum of a biological system



Typical IR
absorbance
positions:

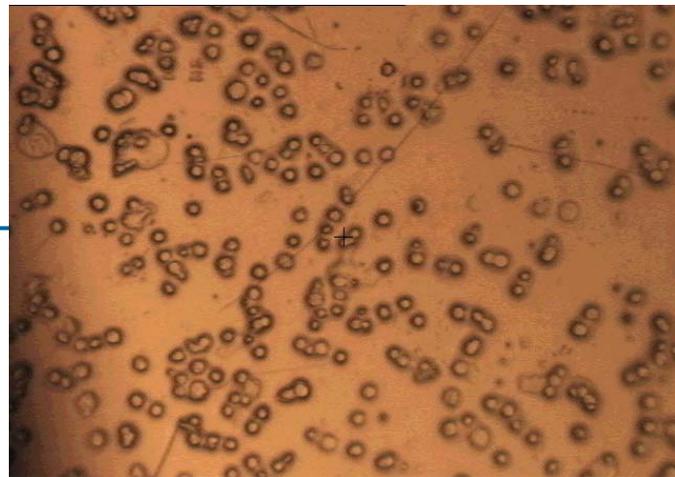
Protein Amide I:	1690-1600
Protein Amide II:	1575-1480
Lipid =CH ₂ :	3100-3000
Lipid -CH ₂ , -CH ₃ :	3000-2850
Nucleic Acid -PO ₂ ⁻ :	1225, 1084

The peak positions of Amide I and II are sensitive to the protein secondary structure (α -helix, β -sheet, random coils, etc.)



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Investigating Individual Living Cells

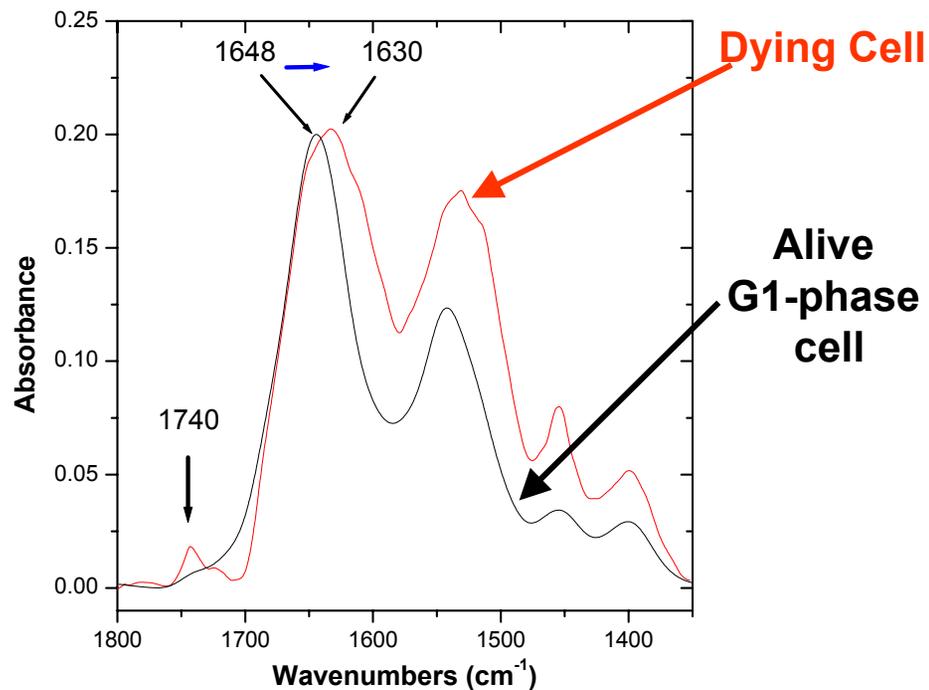
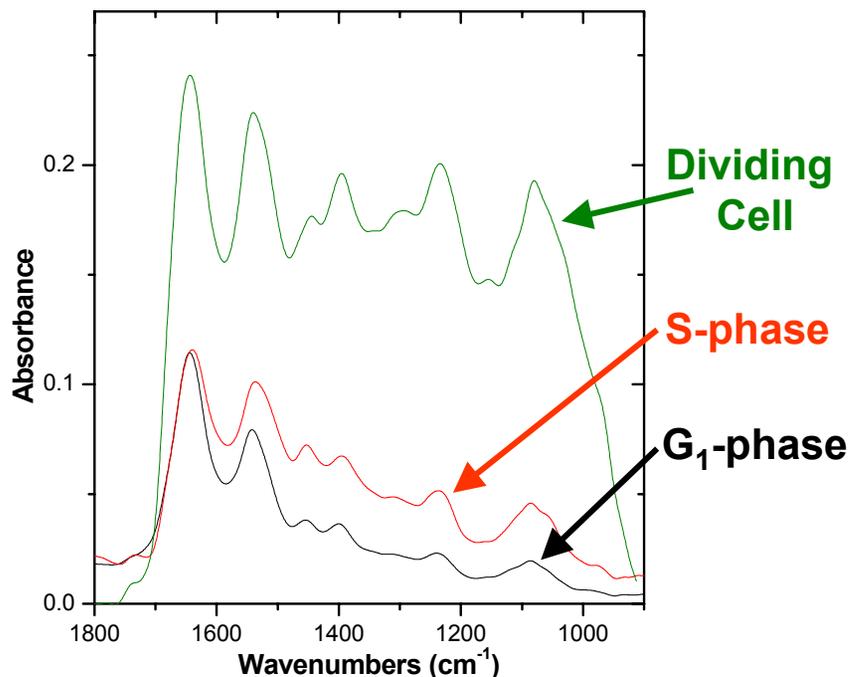


Hoi-Ying N. Holman, *Center for Environmental Biotechnology*

Eleanor A. Blakely, Kathy Bjornstad *Life Sciences Division*

Regine Goth-Goldstein, Marion L. Russell *Environmental Energy Tech. Division*

Michael C. Martin, Wayne R. McKinney, *Advanced Light Source Division*



Lung Fibroblast cells (IMR-90)

ALS Beamline 1.4.3



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Testing the Conventional Understanding of Cellular Responses to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

Intracellular responses to dioxin or aromatic hydrocarbon (PAH) compounds: CYP1A1 protein - a global biomarker of exposure

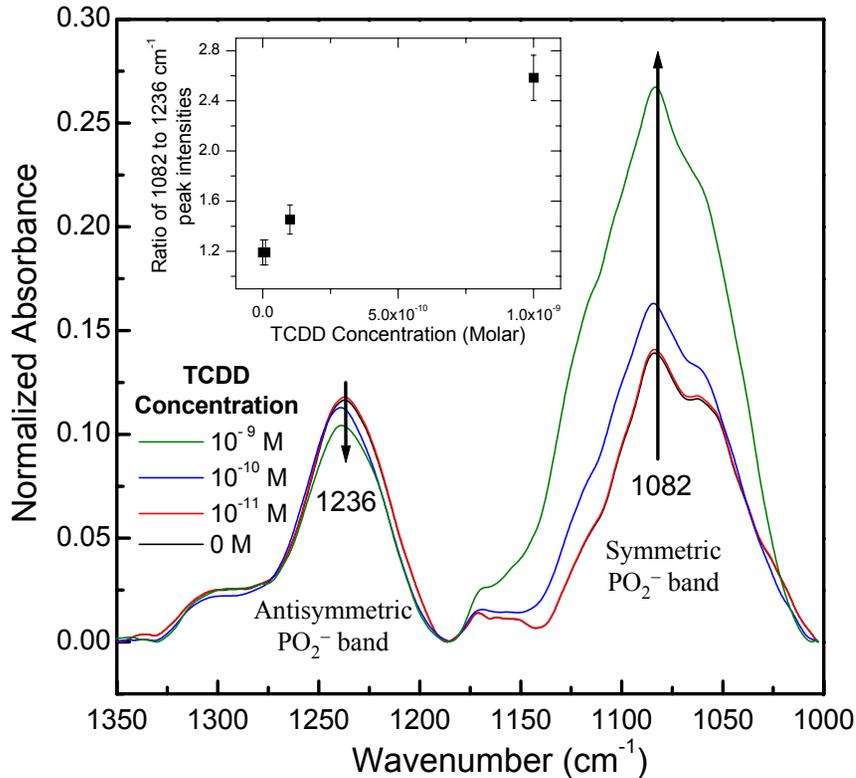
Hoi-Ying N. Holman, *Center for Environmental Biotechnology*, Eleanor A. Blakely, Kathy Bjornstad *Life Sciences Division*
Regine Goth-Goldstein, Marion L. Russell *Environmental Energy Tech. Division*
Michael C. Martin, Wayne R. McKinney, *Advanced Light Source Division*



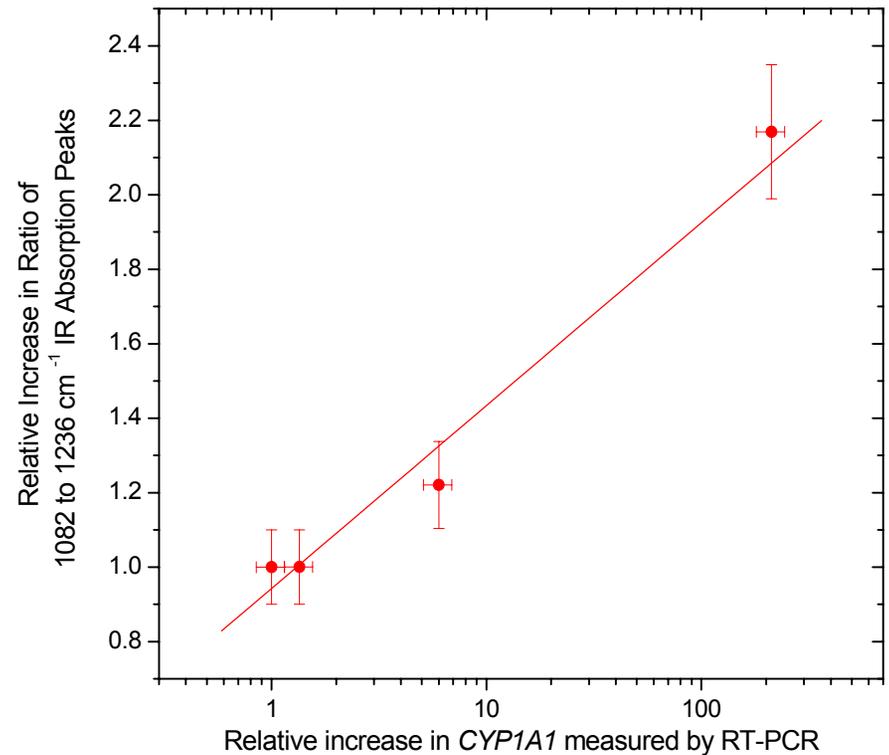
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SR-FTIR Measures Cellular Responses to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

Trypsinized HepG2 cells on gold (37°C)



Nucleic acid spectral region:
Ratio of symmetric to anti-symmetric band
increases with increasing TCDD,
but no shift in peak positions



The observed PO_2^- infrared bands' intensity
changes correlate with the relative
increase in *CYP1A1* expression.

Hoi-Ying N. Holman, Center for Environmental Biotechnology, Eleanor A. Blakely, Kathy Bjornstad Life Sciences Division

Regine Goth-Goldstein, Marion L. Russell Environmental Energy Tech. Division

Michael C. Martin, Wayne R. McKinney, Advanced Light Source Division

ALS Beamline 1.4.3

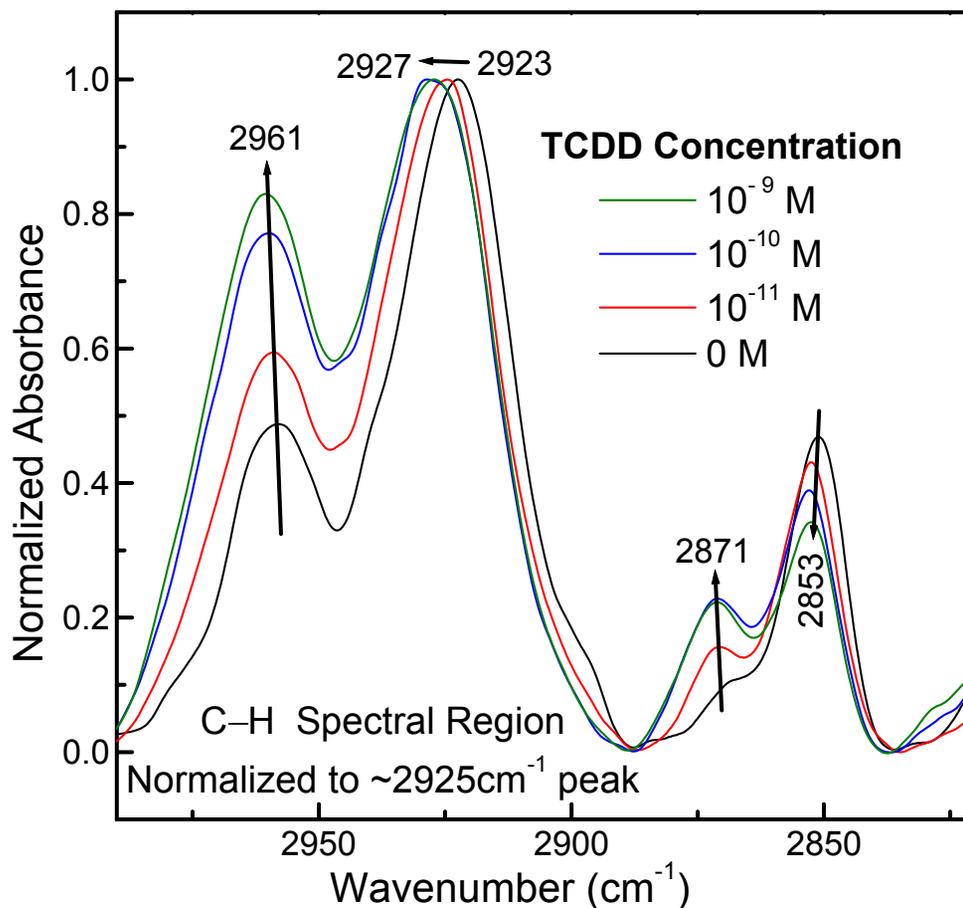


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Comparison of TCDD response measured by SR-FTIR and RT-PCR

C–H stretch region:
Relative increase in number of
methyl to methylene groups
with increasing TCDD.

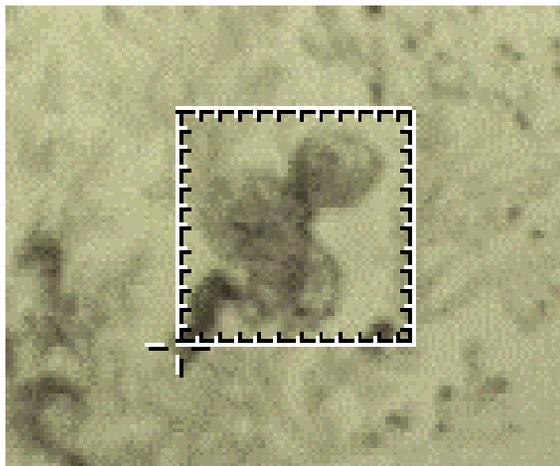
**Methylation occurs but
does not inhibit CYP1A1
expression.**



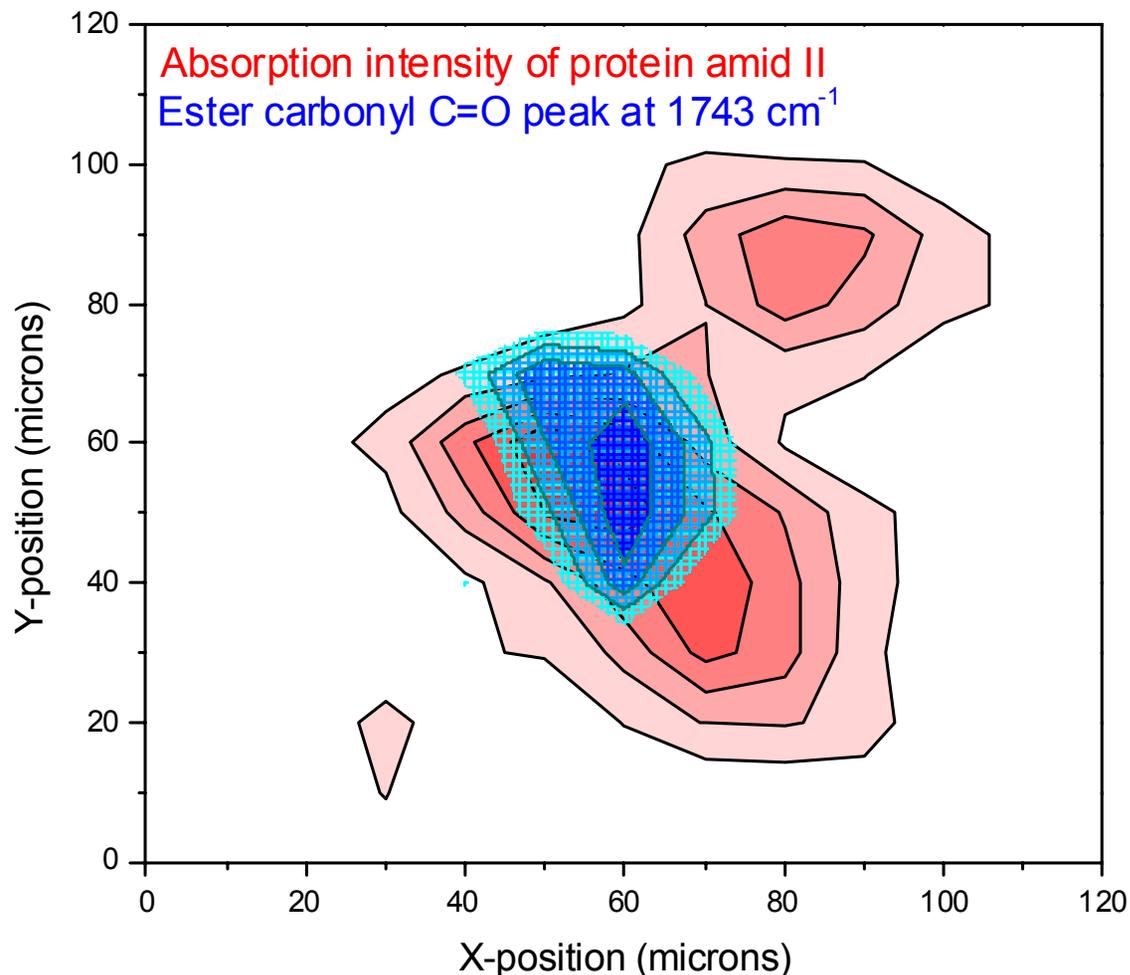


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Imaging the Response of Prostate Cancer Cells to Chemical Treatments



4 hour treatment
with a model
chemotherapy.
IR maps are
measured in-
vitro, in real time



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Enhancing Microbial Bioremediation on Mineral Surfaces

Hoi-Ying N. Holman¹, Dale L. Perry¹, Michael C. Martin¹,
Wayne R. McKinney¹, Jennie C. Hunter-Cevera¹, Karl Nieman²,
Darwin L. Sorensen², Charles D. Miller³, Thomas Borch⁴, Ronald C. Sims²

¹Lawrence Berkeley National Laboratory, Berkeley, CA

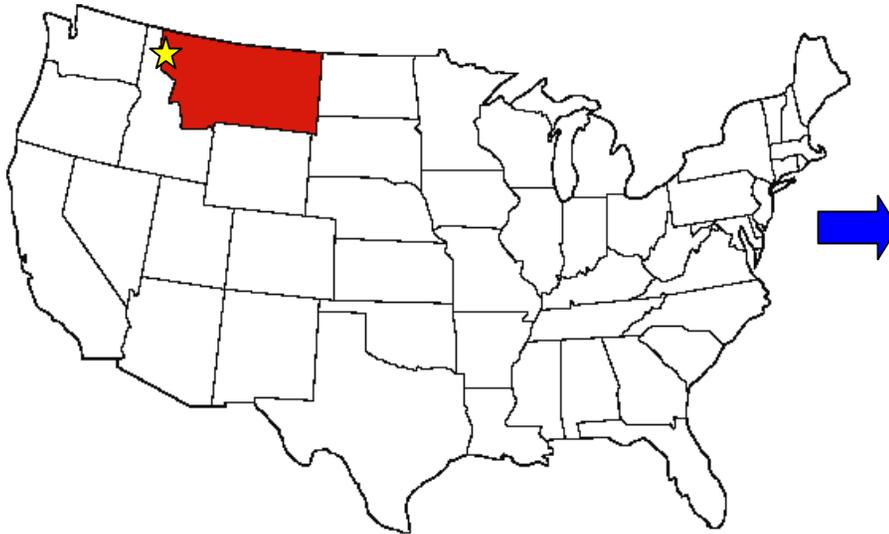
²Utah Water Research Laboratory, Logan, UT

³Utah State University, Logan, UT

⁴Center for Biofilm Engineering, Montana State University, Bozeman, MT

Support thanks: DOD, DOE, EPA, & USGS.

Libby Superfund Site, Montana



1. Placement of contaminated soil into the Land treatment Unit



2. Land treatment Unit during soil treatment

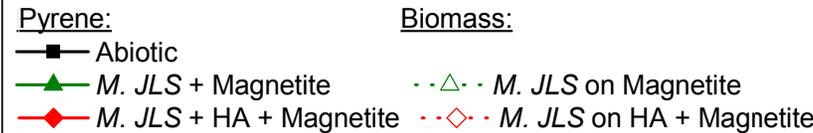
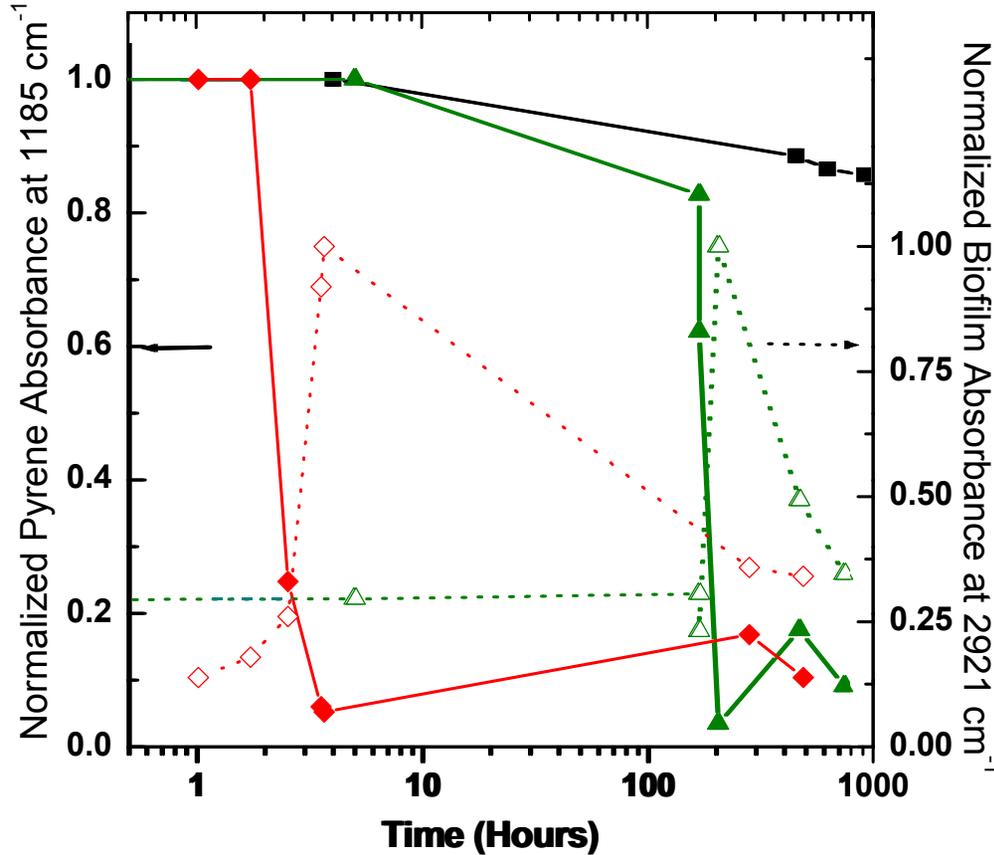
- Can intrinsic bacteria detoxify polycyclic aromatic hydrocarbons (PAH)?
- How can one accelerate this detoxification process?



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Monitoring pyrene biodegradation by SR-FTIR spectromicroscopy

In situ measurements of bacteria metabolizing pyrene on geological surfaces.



The long time lag is for the bacteria to produce enough surfactant-like biomolecules (such as glycolipids).

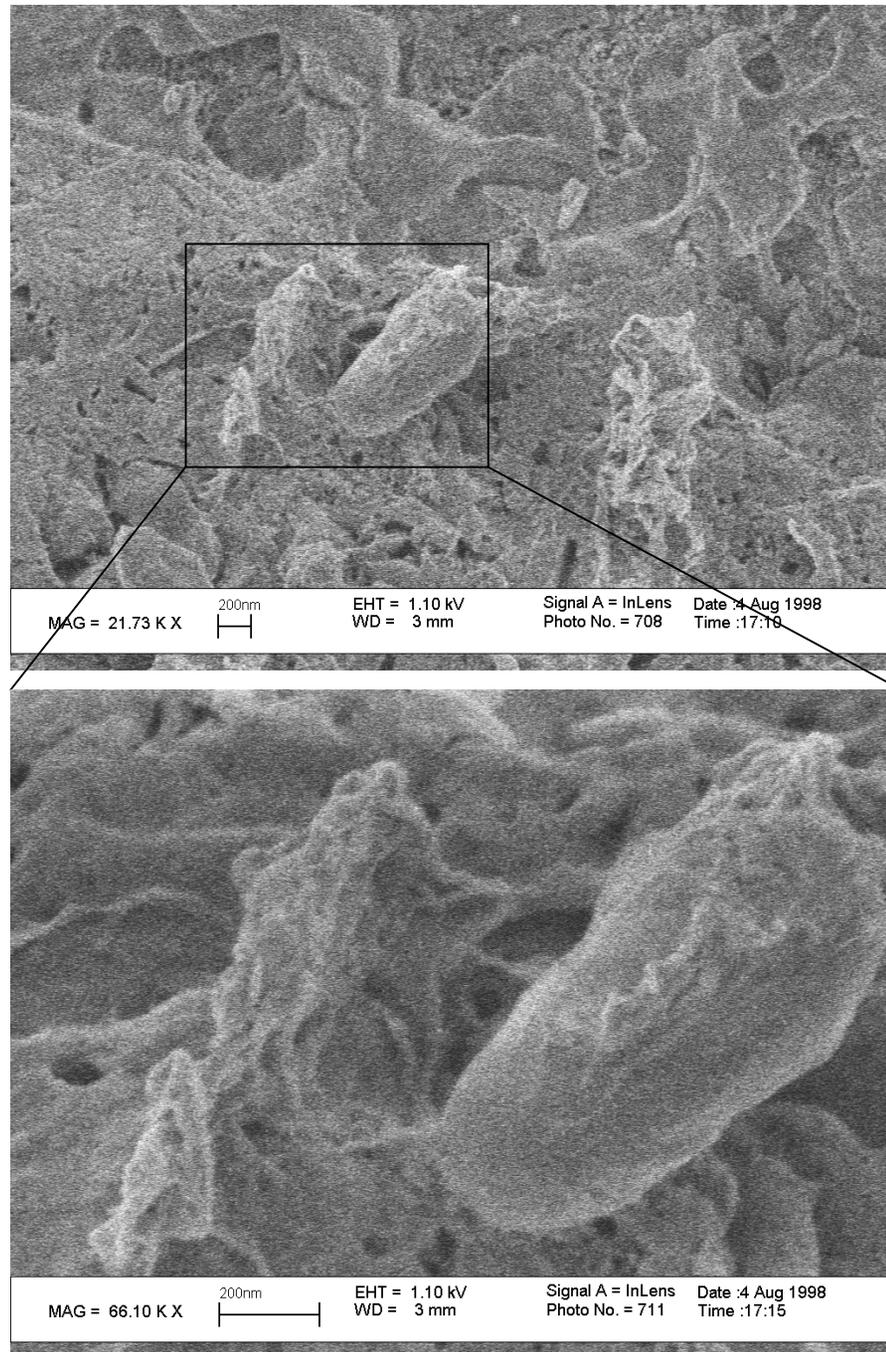
Biodegradation of pyrene is sped up from 200 hours to 2 hours by adding humic acid!



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*Arthrobacter
oxydans*
bacteria
isolated from a
contaminated
DOE site in
Idaho

Scanning
Electron
Microscope
Photos





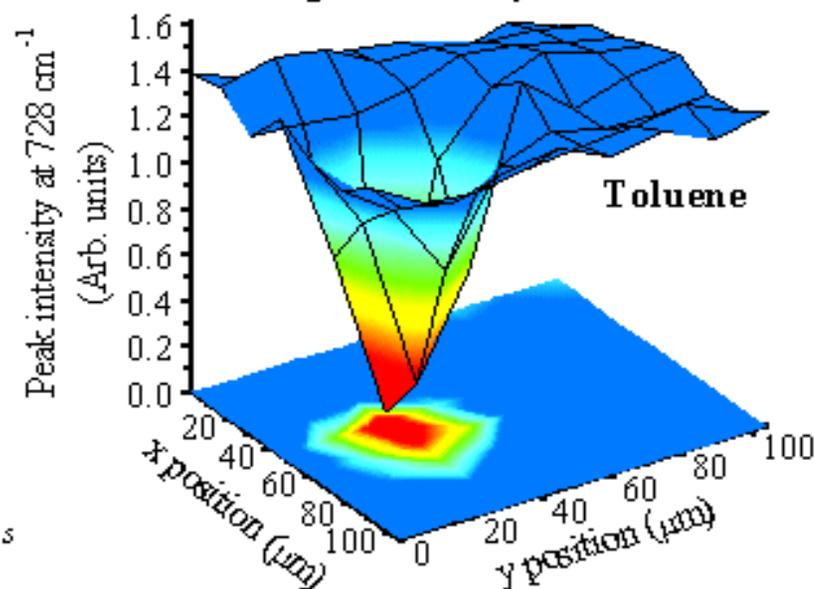
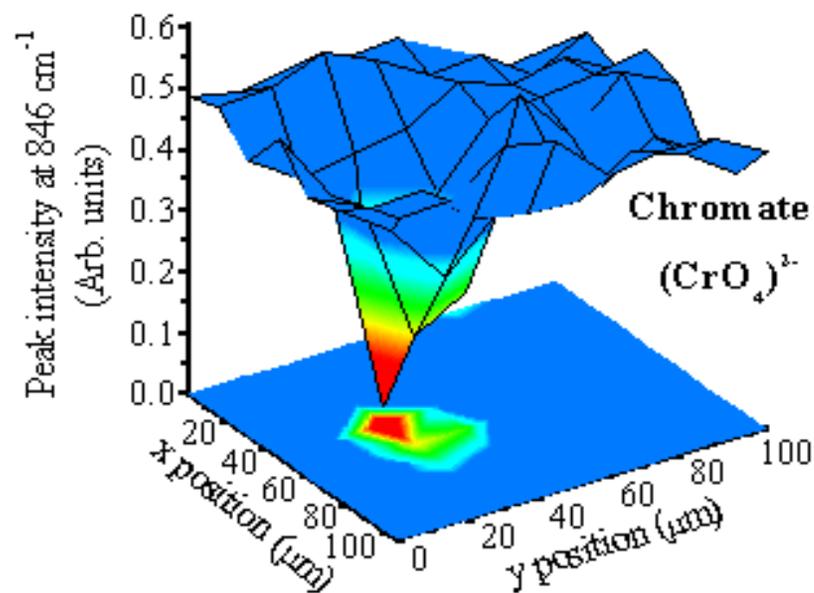
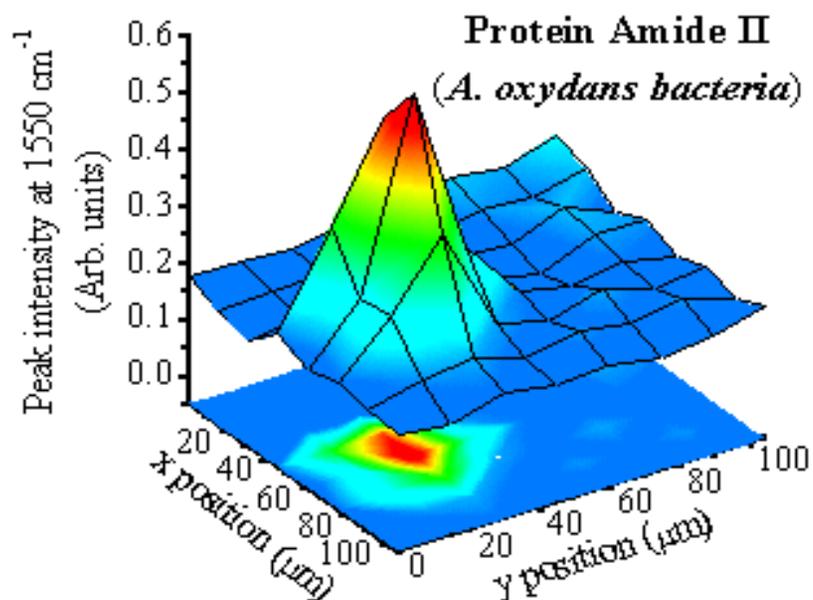
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Infrared Spectromicroscopy Observing

Bacterial Remediation of Environmental Contaminants

ALS Beamline 1.4.3

Hoi-Ying N. Holman, Dale L. Perry, Michael C. Martin
Wayne R. McKinney, and Jennie C. Hunter-Cevera
Lawrence Berkeley National Laboratory



Arthrobacter oxydans bacteria, isolated from a contaminated DOE site in Idaho, attach themselves to magnetite mineral surfaces. We locate the bacteria via their spectral signature (above). We observe a depletion of chromate and toluene (right) by the bacteria after five days of exposure. In this study we will learn how to help *A. oxydans* perform this bioremediation.



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Infrared Spectromicroscopy Observing

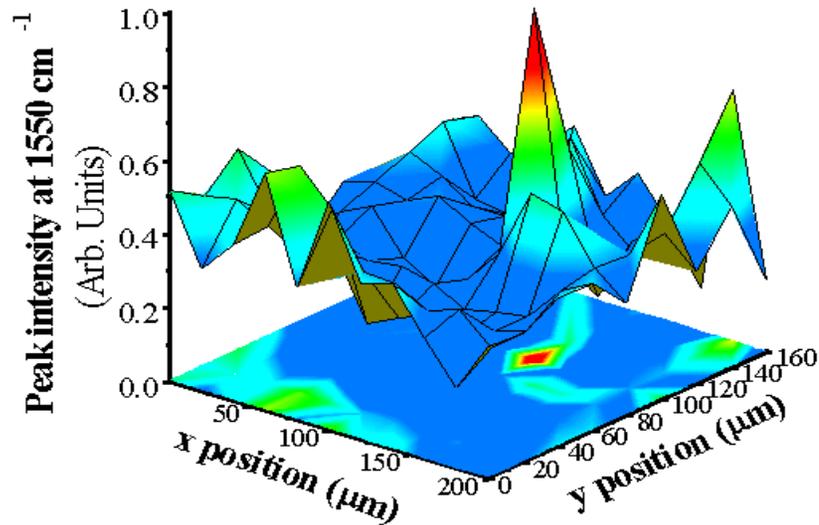
Microbial Reduction of Cr^{6+} to Cr^{3+}

Hoi-Ying N. Holman, Dale L. Perry, Michael C. Martin

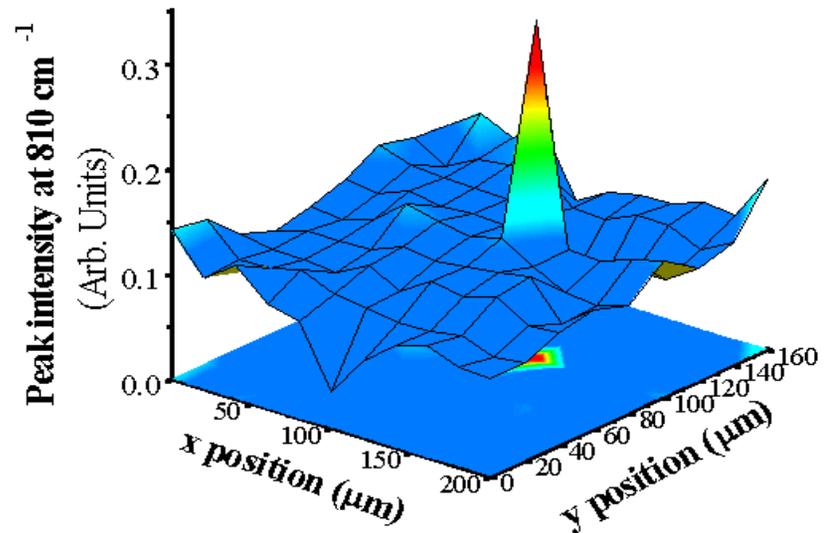
Wayne R. McKinney, and Jennie C. Hunter-Cevera

E.O. Lawrence Berkeley National Laboratory

Protein Amide II
Indigenous Microorganisms



Cr^{3+} compounds

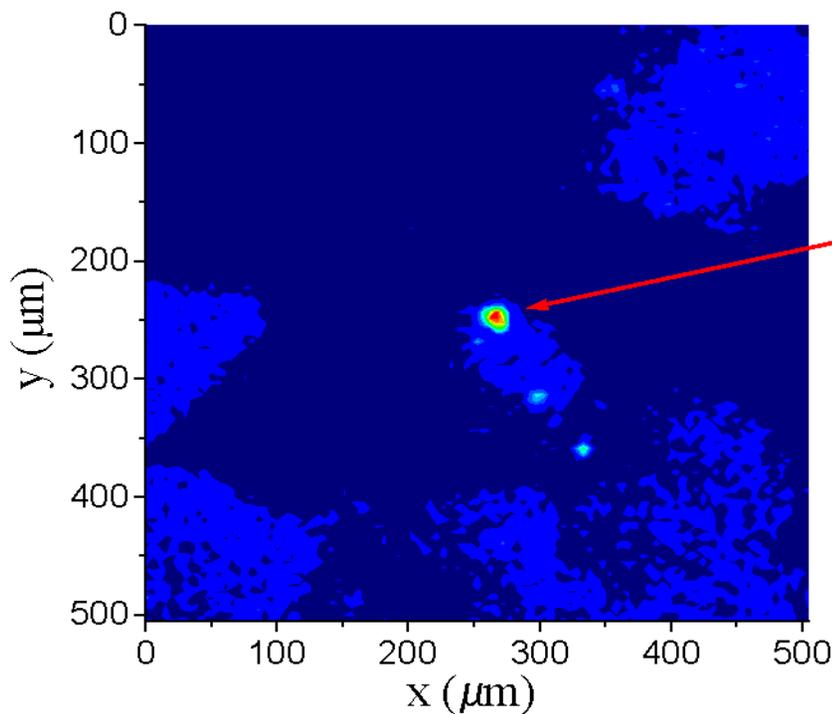


Indigenous microorganisms found on vesicular basalt surfaces are located by their IR spectral signature (left figure). We observe a reduction of chromate (Cr^{6+}) to Cr^{3+} compounds by the microorganisms after four months of exposure in the presence of dilute toluene vapor (right). In this study we will learn how to help intrinsic microorganisms perform this metal bioremediation.

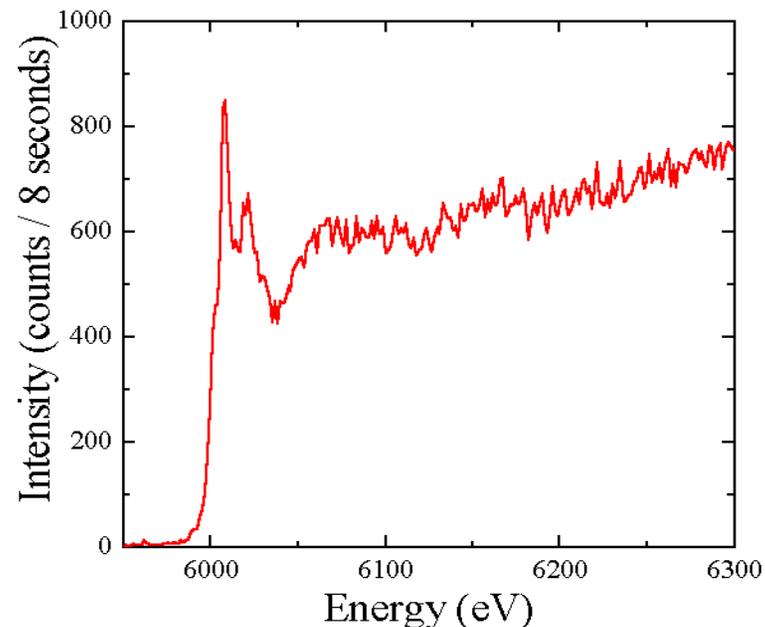
**Advanced Light Source
Beamline 1.4.3**

Confirmation of Cr^{3+} by Micro-x-ray Analysis

Same sample as studied by infrared spectromicroscopy



Chromium elemental mapping



**XAFS scan showing Chromium
peak in map is indeed Cr^{3+}**

Geraldine Lamble

E.O. Lawrence Berkeley National Laboratory

Advanced Light Source

Beamline 10.3.2



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High-Impact Infrared Science

Some recent **Science & Nature** references

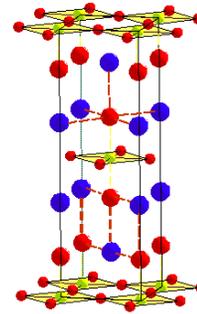
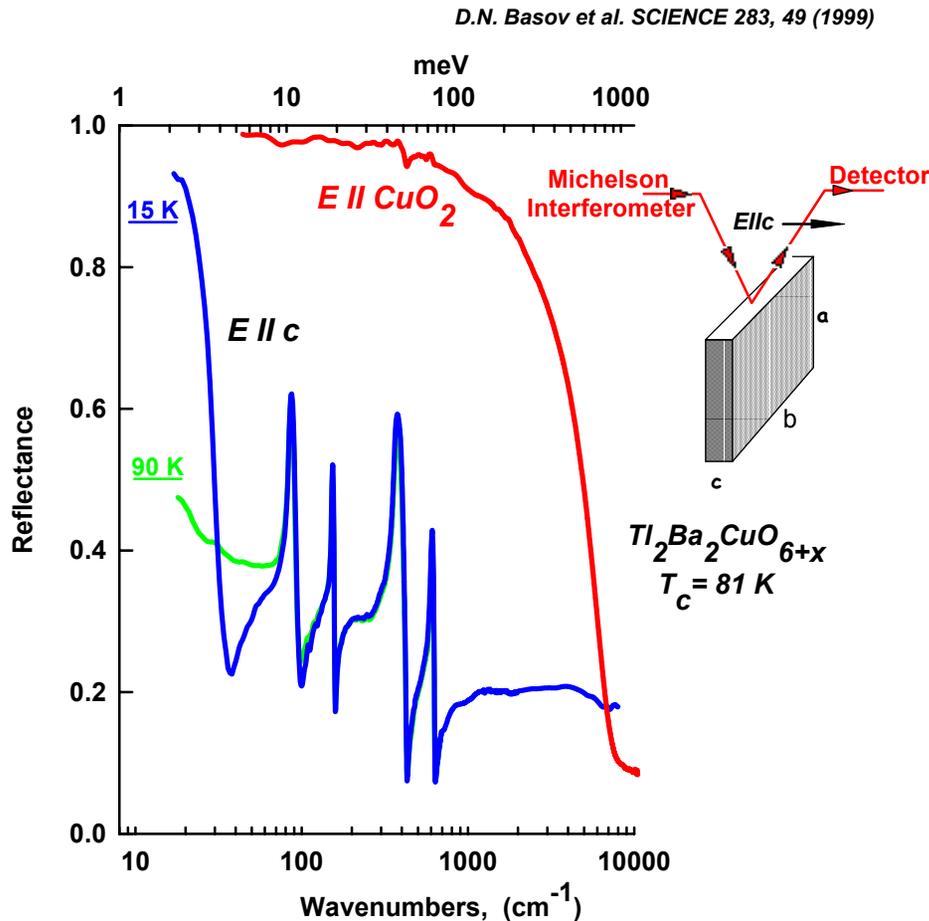
- 1999-2001: **23 Science & 18 Nature papers** using infrared spectroscopy
- A Recent review: Science **285**, 1224 (1999).
- **Solid state physics:** High- T_c 's, CMR, Ruthenates, complex oxides, ...
Science **293**, 673 (2001)*, Nature **414**, 286 (2001), Nature **404**, 373 (2000), Science **287**, 470 (2000)*, Nature **401**, 351 (1999)*, Science **283**, 49 (1999)*, Nature **398**, 221 (1999)*, Science **281**, 1181 (1998)*.
- **Nanotechnology:** Nanocrystals, Nanotubes, Qubits...
Science **291**, 2390 (2001), Nature **414**, 289 (2001), Nature **410**, 60 (2001), Nature **407**, 981 (2000), Science **288**, 313 (2000), Science **287**, 633 (2000)*, Science **287**, 839 (2000), Science **282**, 95 (1999), Nature **391**, 466 (1998)*.
- **Biological & Biomedical:** Protein folding, Phototrophy, Bio-sensors ...
Nature **405**, 586 (2000), Nature **405**, 810 (2000), Science **289**, 1902 (2000), Science **288**, 859 (2000).
- **Environmental Applications:** Bioremediation, Carbon cycle, ...
Science **292**, 2492 (2001), Nature **405**, 60 (2000), Nature **404**, 861 (2000), Science **274**, 582 (1996).
- **Chemistry:** Molecular clusters, rotational spectroscopy, polymers...
Science **295**, 482 (2002)*, Science **292**, 481 (2001), Nature **412**, 423 (2001), Nature **409**, 794 (2001), Science **289**, 1532 (2000), Science **287**, 2461 (2000), Science **287**, 5451 (2000), Science **284**, 945 (1999)*, Science **284**, 135 (1999).
- **Surface science:** adsorbate / substrate interactions, interfaces ...
Science **293**, 1811 (2001), Nature **409**, 1023 (2001), Science **292**, 481 (2001), Nature **404**, 281 (2000), Nature **404**, 376 (2000), Science **279**, 679 (1998).
- **High-pressure research:** Geophysics, entirely new phases, ...
Nature **411**, 170 (2001)*, Science **288**, 1215 (2000), Nature **404**, 240 (2000)*, Science **286**, 100 (1999)* Science **273**, 218 (1996)*.

* = Papers by IR Ring Supporters

Scientific Examples: High-Temperature Superconductors

P.W. Anderson (1991): Two “**smoking guns**” for High- T_c Superconductivity:
“Angle-resolved photoemission ... and absorption of c-axis polarized infrared”

Cuprates: anisotropic reflectivity



“The point is that interesting features in the c-axis response are in VERY far infrared $< 50 \text{ cm}^{-1}$. We pushed conventional sources to the limit to get this data. Synchrotrons may help to advance to even lower energies.”

-Prof. Dimitri Basov, UCSD

Science **283**, 49 (1999)

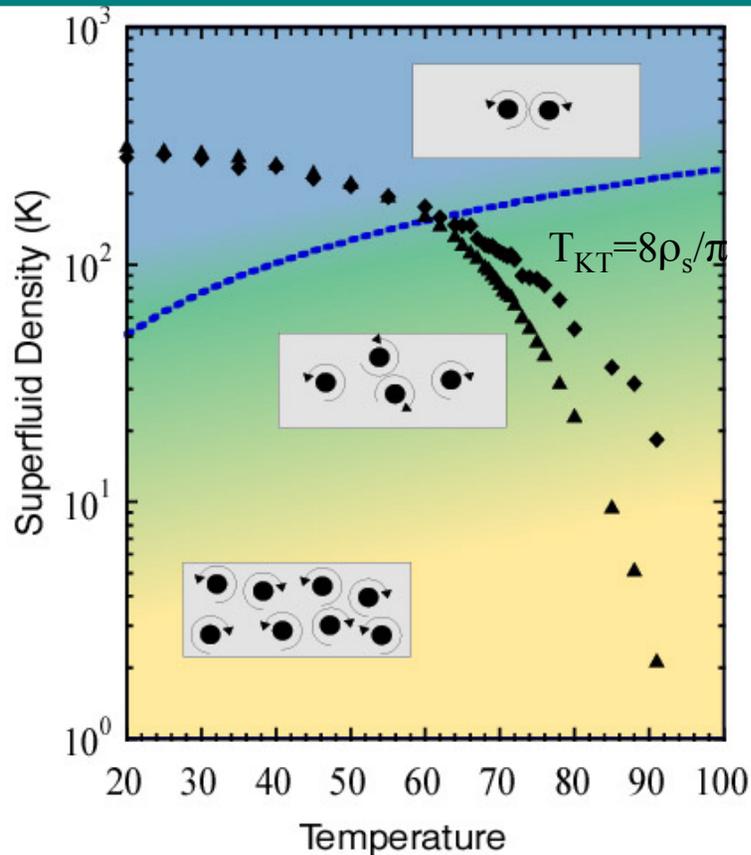
Nature **401**, 351 (1999)

Phys. Rev. Lett. **86**, 684 (2001)



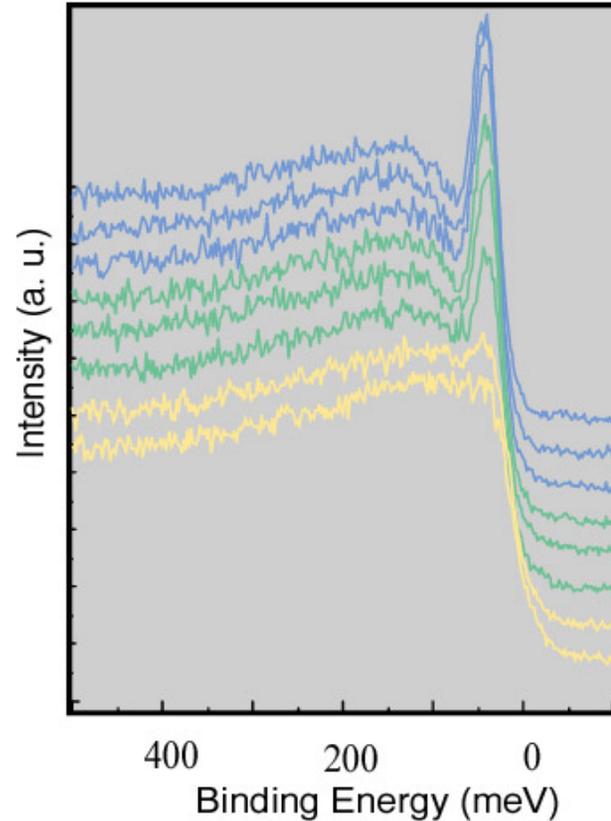
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Far-IR & Photoemission Complementarity



“Vanishing of phase coherence in underdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ”

J. Corson, R. Mallozzi, J. Orenstein, J. N. Eckstein & I. Bozovic, **Nature** 398, 221 - 223 (1999)



“Excitation Gap in the Normal State of Underdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ”

A. G. Loeser, Z.-X. Shen, D. S. Dessau, D. S. Marshall, C. H. Park, P. Fournier, A. Kapitulnik **Science** 273, 325-329 (1996).

As the phase stiffness disappears, so do the quasiparticles?

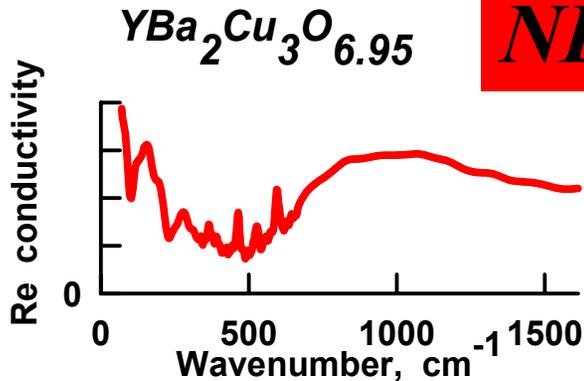
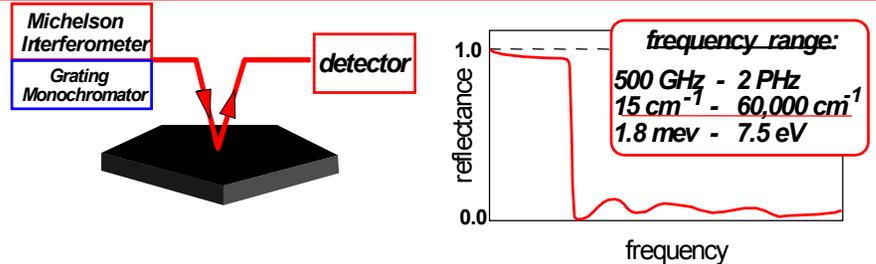
Coupling of Charge Carriers to Magnetic Resonance: a Path to high- T_c Superconductivity?

MAGNETIC RESONANCE:

- Signature of superconducting state
- $E = 40 \text{ meV}$, $q = (\pi/a; \pi/a)$
- E scales with T_c
- YBaCuO and BiSrCaCuO
- *Coupling to charge carriers?*

D.N. Basov (UCSD)

Experiment: IR reflectance measurements

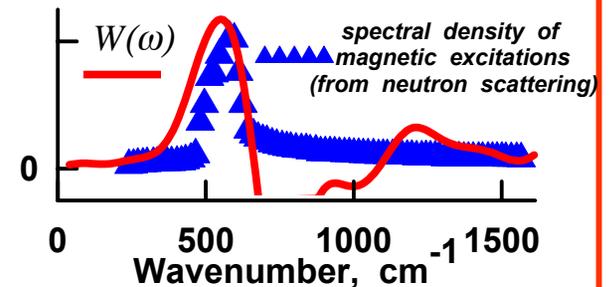


NEW ANALYSIS

$$W(\omega) = \frac{1}{2\pi} \frac{d^2}{d\omega^2} \left[\omega \operatorname{Re} \frac{1}{\sigma(\omega)} \right]$$

NATURE 401, September 23, 1999

J.P. Carbotte, E. Schachinger, D.N. Basov



KEY RESULTS

- Charge carriers in YBaCuO are coupled to 40 meV magnetic resonance
- Coupling strength is sufficient to account for high critical temperature

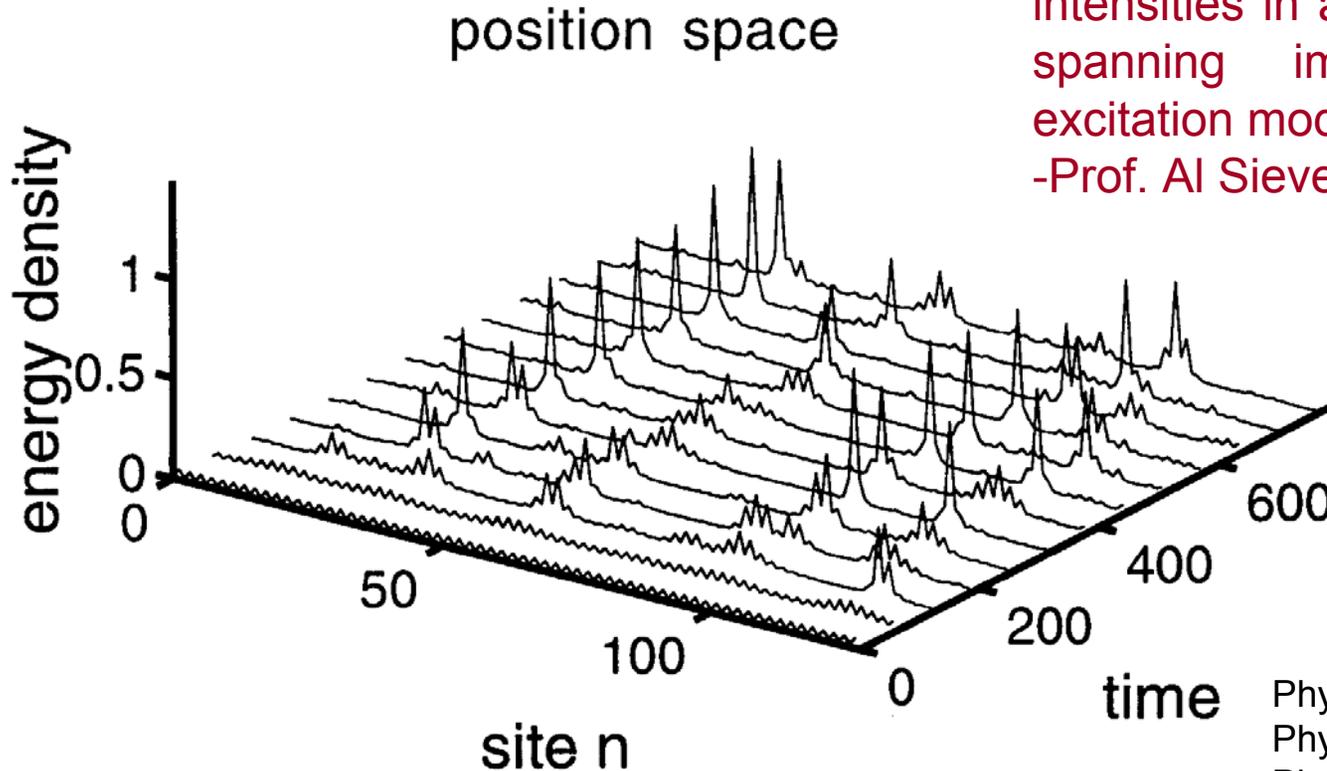


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Non-linear effects with high power IR

Intrinsic Localized Modes: Driven non-linear motion of atoms within a lattice with very large displacements & which remain localized.

“Coherent radiation from 300 fs bunches would produce high intensities in a wavelength region spanning important collective excitation modes of solids.”
-Prof. Al Sievers, Cornell

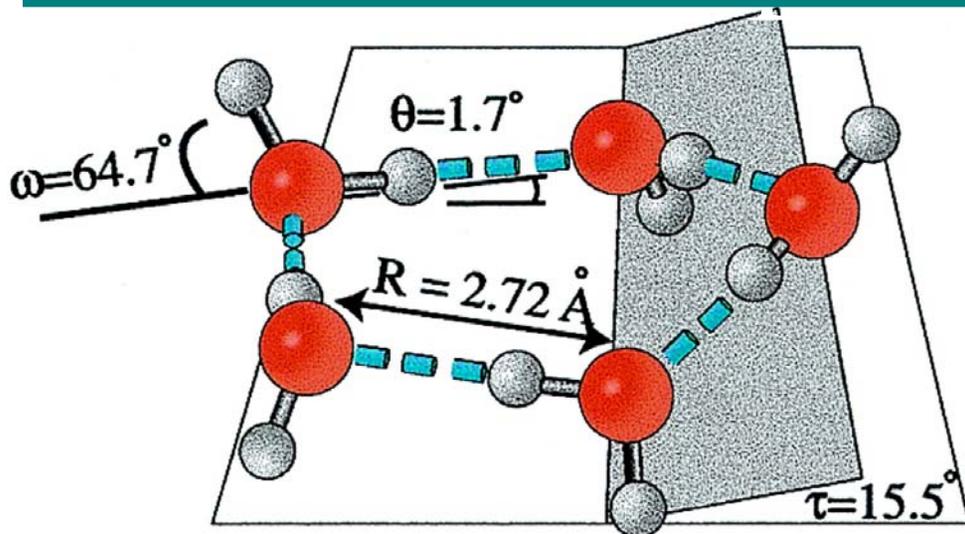


Phys. Rev. Lett. **83**, 223 (1999)
Phys. Rev. Lett. **81**, 3687 (1998)
Physics Reports **314**, 147 (1999)



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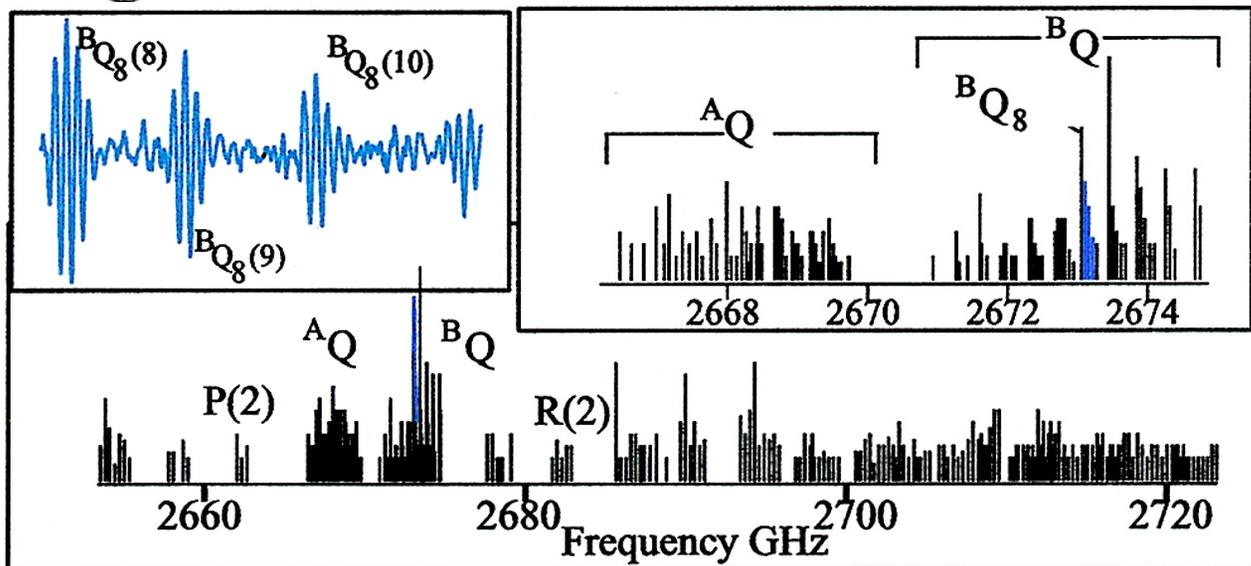
Vibrational-Rotational-Tunneling Spectroscopy



Rich Saykally, UCB
Extremely high resolution:
4.6 MHz (0.00015 cm^{-1}) splittings
Very difficult far-IR measurements

More measurements:

- Proton Transfer
- Amino Acids
- Nucleotide Bases
- Water Clusters

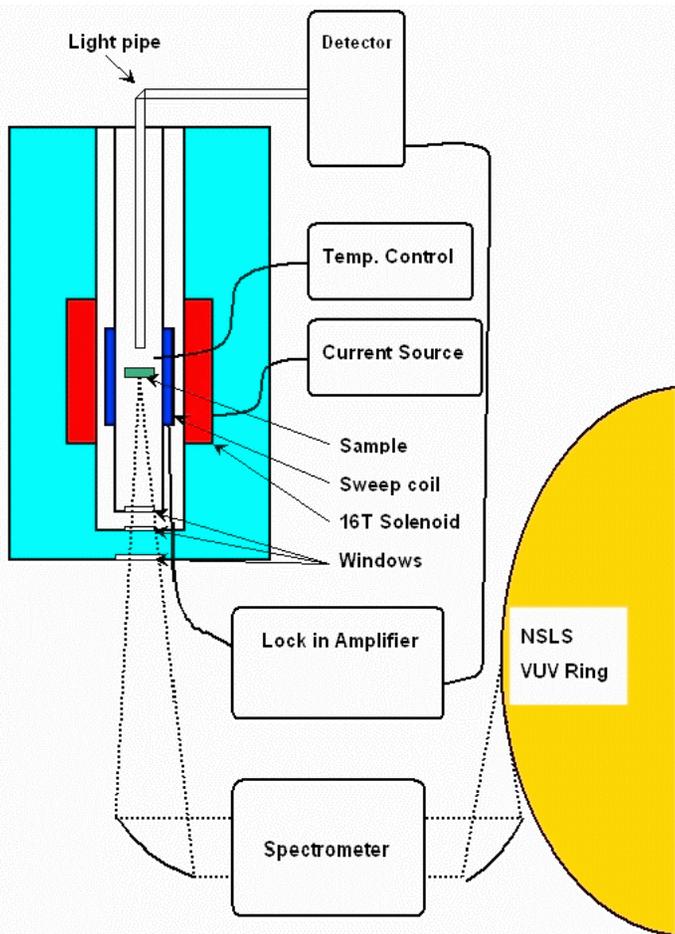


Synchrotron-based Electron Spin Resonance (ESR) Spectroscopy

Traditional ESR: Single fixed frequency setups.

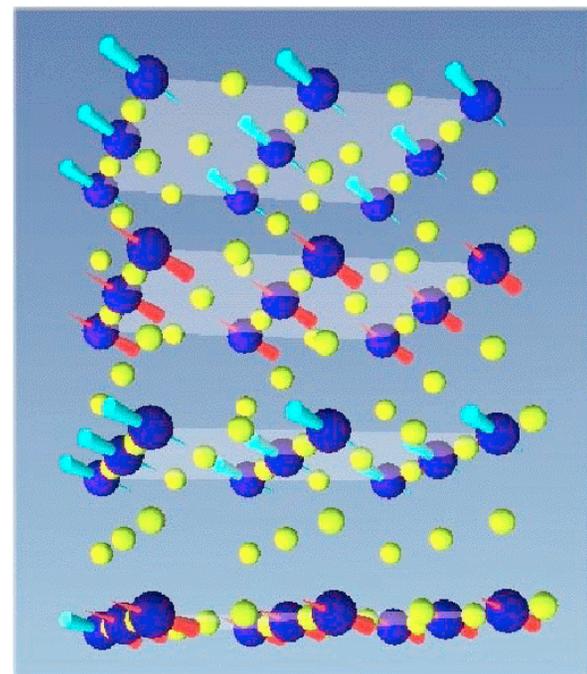
New concept: Combine high-flux far-IR & high-field magnets.

First demonstration measurements in 2001 at the NSLS – still need much more far-IR flux!



LaMnO₃:

Parent to CMR's,
Mn sites have
localized spins,
Antiferromagnetic
ordering at 145K.

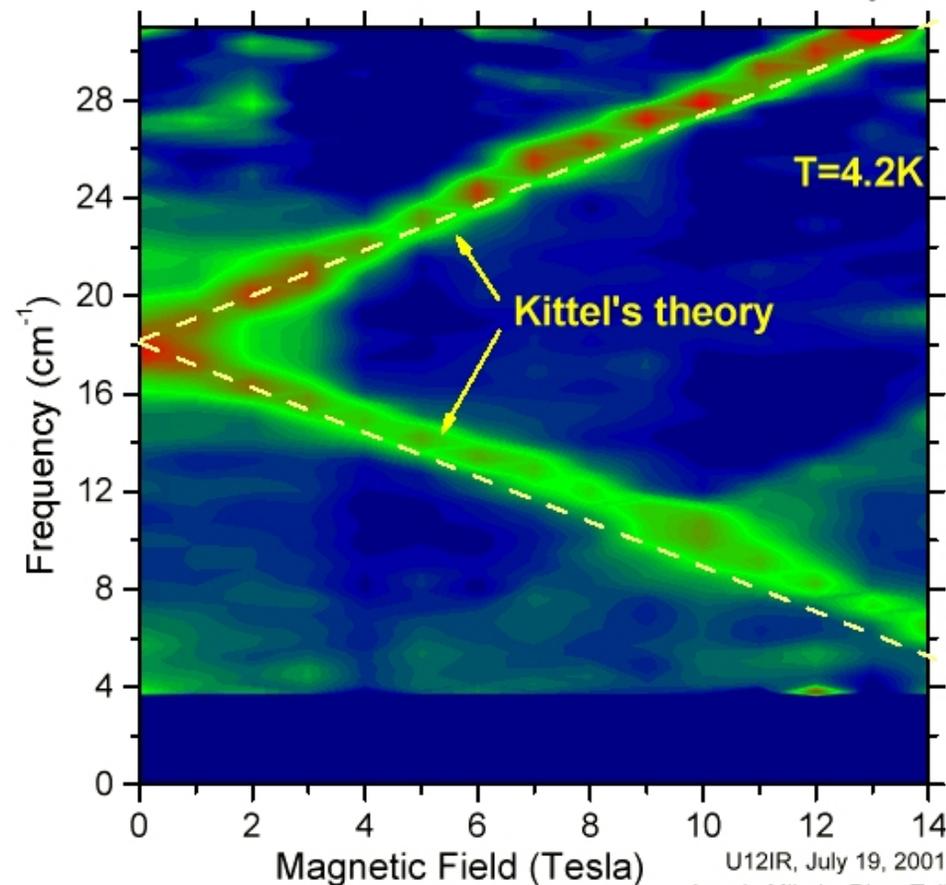




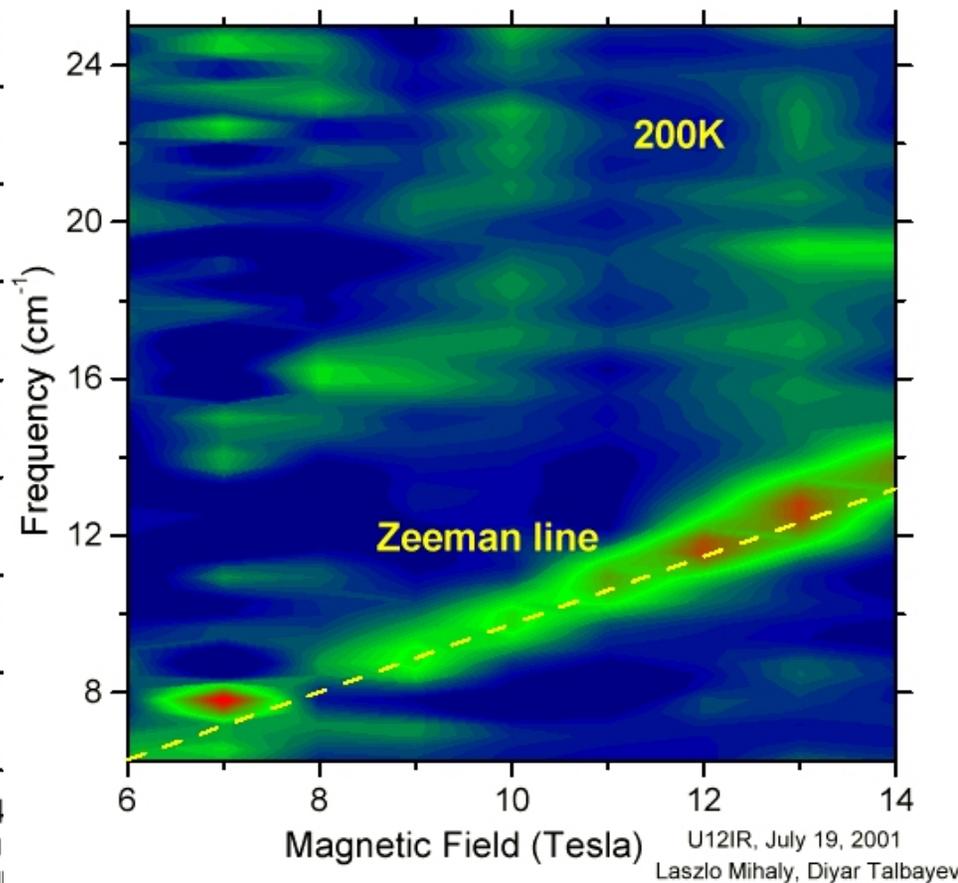
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Synchrotron-based Electron Spin Resonance (ESR) Spectroscopy

Antiferromagnetic Resonance in LaMnO_3



Electron Spin Resonance in LaMnO_3

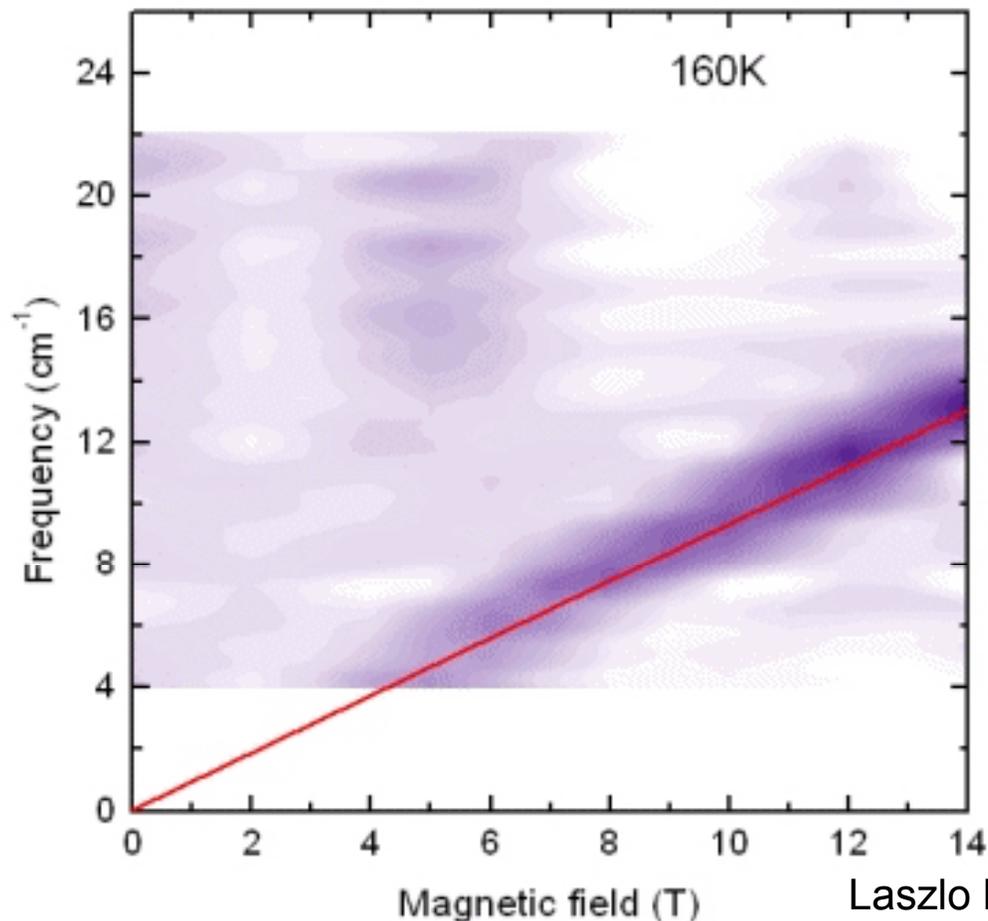




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Synchrotron-based Electron Spin Resonance (ESR) Spectroscopy

Transition from high to low temperature (AF ordering at 145K):

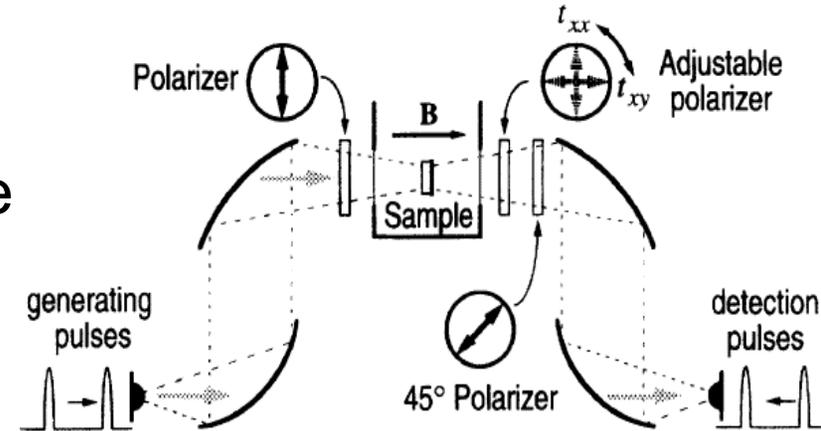


Laszlo Mihaly & Diyar Talbayev
February 2002

EO Sampling with Synchrotron Source?

Electro-optic sampling is a powerful tool of THz spectroscopy:

- Measures phase and amplitude
- Time-domain measurements for dynamics
- Imaging & tomography

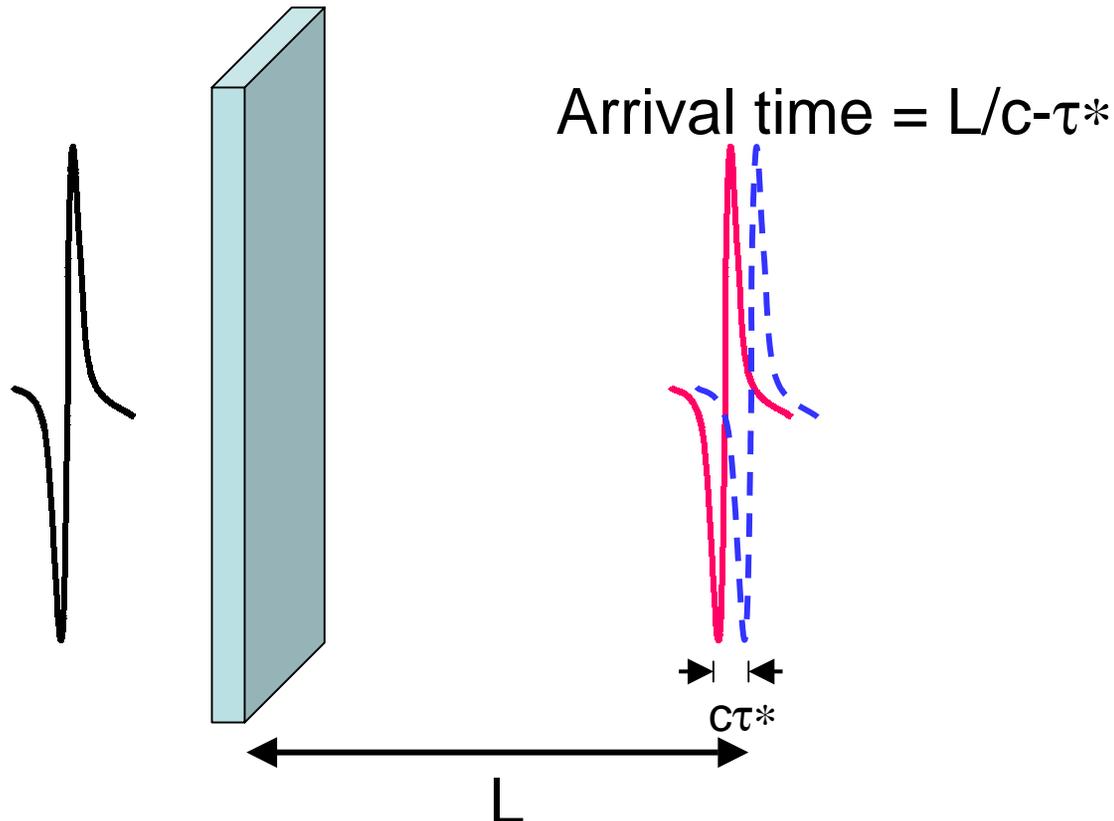


Possibly we can use the synchronized visible synchrotron pulse as the probe for an EO setup.

Or failing that, synchronize a laser to the storage ring. Try using the laser oscillator as the frequency source for the ring RF system. Might be able to phase-lock the visible synchrotron pulses to the laser.

EO Sampling with Synchrotron Source?

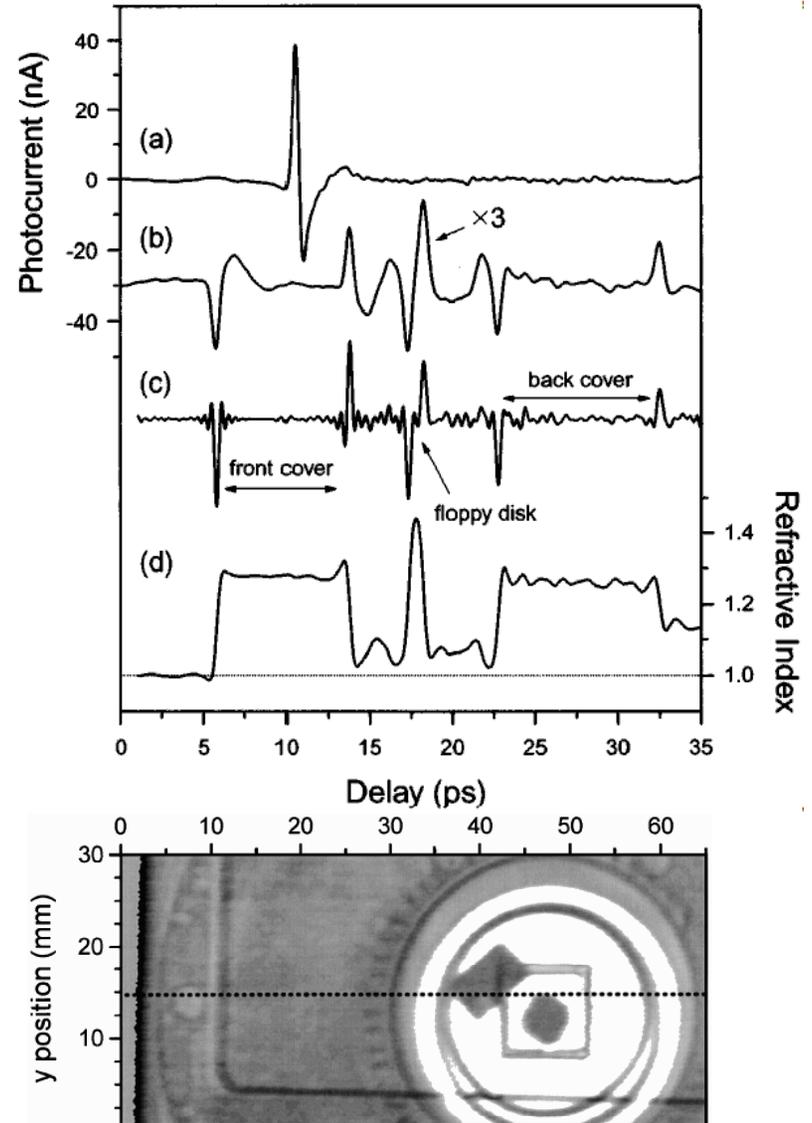
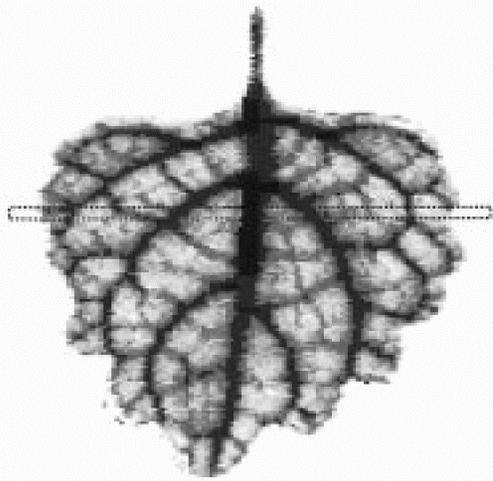
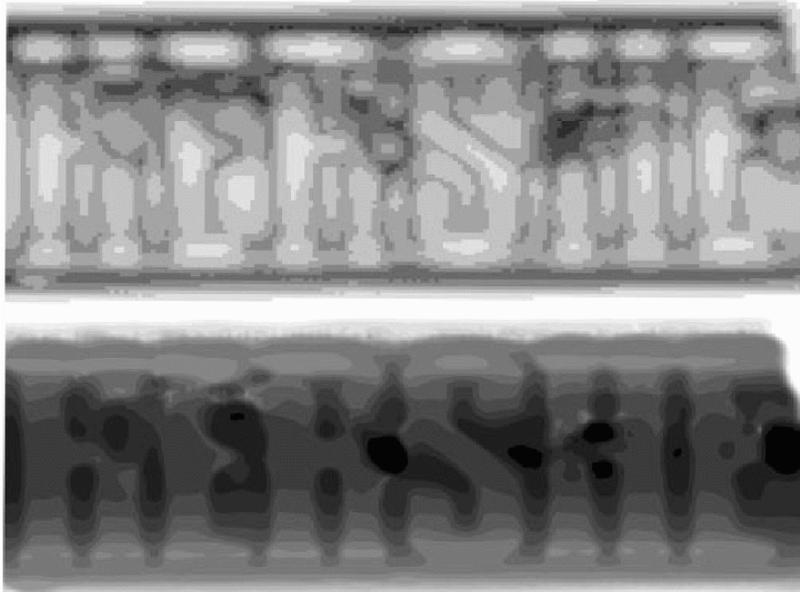
Time-domain measurements for dynamics





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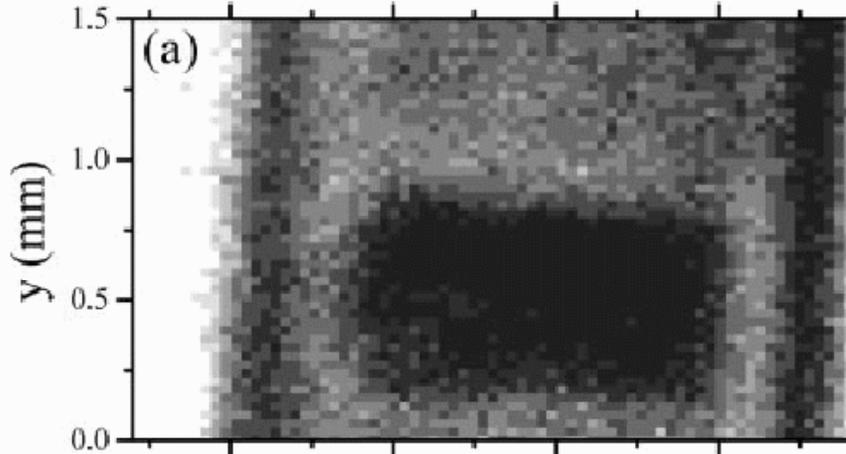
THz Imaging



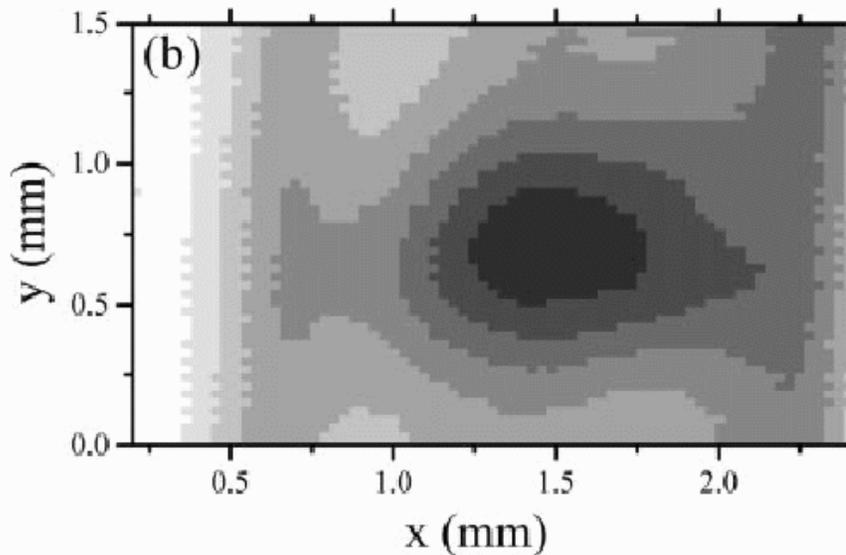


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THz Near-Field Imaging



← 100 micron aperture image.



← Regular THz image.

Near-field is very lossy,
 10^5 loss is typical.

Therefore high-flux is key!



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Scientific Community Support for a Dedicated Far-IR Synchrotron

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Saykally, Richard (UC Berkeley)
Schade, Ulrich (Berlin)
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Sievers, Al (Cornell)
Sigee, David (U. Manchester)
Smith, Todd (Stanford)
Timusk, Tom (McMaster U.)
Williams, Gwyn (Jefferson Lab)
Wolkers, Willem (UC Davis)



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Upcoming Workshops

WIRMS 2003

International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources

July 8-11, 2003, Lake Tahoe, CA



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Chairs:

Michael C. Martin (ALS, LBNL)

Todd I. Smith (HEPL, Stanford)

Wayne R. McKinney (ALS, LBNL)

Daniel Palanker (HEPL, Stanford)

<http://infrared.als.lbl.gov/WIRMS/>

Michael C. Martin

